ANNUAL RETENTION OF
AMMONIUM AND NITRATE
AND SHORT-TERM IONIC COMPOSITION
OF STREAMWATER DURING SNOWMELT
IN LAKES AND FORESTED CATCHMENTS
IN ONTARIO

MARCH 1989

Environment Ontario

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Minister

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March 1989

ABSTRACT

The relative contribution of HNO_3 to precipitation acidity in eastern Canada
has increased in recent years leading to some concern that the relative
importance of NO_3^- deposition on acidification of terrestrial and aquatic
ecosystems may increase. To gauge the extent of this impact, annual mass
balances for NO_3^- and NH_4^+ were calculated for several forested catchments
and lakes in Ontario. Retention of NH_4^+ (R_{NH_4}) by forested catchments
was consistently high compared to retention of NO_3^-, (R_{NO_3}). Retention
of TIN (NH_4^+ + NO_3^-) appeared to be influenced more by annual areal
water discharge rate than by NO_3^- deposition. The reciprocals of retention
of NO_3^-, NH_4^+ and total inorganic N by lakes were linearly related to the
ratio of lake mean depth to water residence time ($\bar{z}/\tau$; equal to areal
water discharge rate) and retention did not appear to be a function of N
deposition or degree of acidification of the lakes. Net N consumption-based
acidification of lakes, defined as the ratio of annual NH_4^+ to NO_3^-
consumption, was highly negatively correlated with $\bar{z}/\tau$ and was most
likely to occur when $\bar{z}/\tau$ was <1.5 m yr^{-1}.

Although site-specific changes in loading will not alter the proportions
retained and exported, at least within the range of loadings for the systems
reported here, changes in loading will result in changes in the absolute
amounts of inorganic N retained and exported. Hence, increased NO_3^-
deposition will result in higher NO_3^- concentrations and greater acidity in
stream and lake waters, and decreased deposition should result in increased
alkalinities. Systems with high areal water discharge rates appear most
susceptible to changes in deposition.

The relative contributions of changes in base cations and acid anions to
alkalinity decreases during spring snowmelt in 1984-86 were analyzed for 15
headwater streams and lake outflows in three central Ontario catchments.
During most episodes, there were partially offsetting concentration changes in
ions which contributed to alkalinity decreases and smaller changes in other
ions which contributed to alkalinity increases. The major contributor to
alkalinity depressions was base cation dilution by snowmelt water.

Depressions were more likely to be dominated by SO_4^{2-} increases as the degree of stream acidification increased. Neither nitrate nor organic acid anions were significant contributors to alkalinity depressions. Discharge was highly correlated with alkalinity in a circumneutral stream but not in an acidic stream.

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INTRODUCTION

Nitrogen oxide emissions in eastern North America and nitrate deposition and
concentration in precipitation in central Ontario have not changed
significantly in the past decade (Dillon et al. 1988). In contrast, SO_x
emissions, deposition and concentrations have decreased, resulting in a
gradual increase in the equivalent ratio of NO_3^- to SO_4^{2-} in deposition in
central Ontario from 0.43 in 1976-77 to 0.68 in 1985-86 (Dillon et al. 1988).
The maximum possible contribution of NO_3^- to precipitation acidity (NO_3^-/H^+)
has also increased in recent years whereas the maximum contribution of SO_4^{2-}
has not changed (Dillon et al. 1988). These trends in deposition have led to
some concern that the relative impact of NO_3^- deposition on acidification of
terrestrial and aquatic ecosystems may increase (McLean 1981; Galloway and
Dillon 1983). Concern has also been expressed about the acidification effects
of N deposition in Europe (Grennfelt and Hultberg 1986).

The contribution of both NO_3^- and NH_4^+ deposition to long-term acidification
is complicated by biological consumption and production which generates or
consumes alkalinity (Brewer and Goldman 1976; Schindler et al. 1985;
Grennfelt and Hultberg 1986). Since NH_4^+ is generally a preferred source of
N for assimilation (Syrett 1981), high NH_4^+ deposition rates may generate
considerable acidity via high NH_4^+ and inhibited NO_3^- assimilation rates.
High NH_4^+ deposition rates in some parts of Europe are considered to be a
major source of acidity (van Breemen et al. 1982). As a further complication,
microbiological processes such as mineralization, denitrification and
nitrification may be affected by acidification and high SO_4^{2-} concentrations
(Strayer et al. 1981; Knowles 1982; Klein et al. 1983).

Mass balance studies show a range of values for retention of NO_3^- by lakes
and catchments (Henriksen and Wright 1977; Likens et al. 1977; Galloway et al.
1980a, 1983; Wright and Johannessen 1980; Kerekes et al. 1982; Wright 1983;

Hemond and Eshleman 1984; Kelly et al. 1987). Sulphate retention by lakes and catchments is usually much lower than NO_3^- retention, indicating less chemical and biological reactivity (Schindler et al. 1976, 1986; Galloway et al. 1980a; Wright and Johannessen 1980; Hemond and Eshleman 1984; Kelly et al. 1987). Processes resulting in retention of NO_3^- within a lake or catchment are considered to generate an equivalent or near-equivalent amount of alkalinity.

In this paper annual NO_3^- and NH_4^+ mass balances for seven subcatchments, two lakes, and two combined lake-catchment systems in central Ontario are reported for eight years (1976-84). The results are compared to those from several lakes and forested stream catchments experiencing a range of N deposition rates in different regions of Canada, in the U.S..A. and in Scandinavia.

STUDY AREA

Harp and Plastic Lakes are located in the Muskoka-Haliburton area of central Ontario (Figure 1). Plastic Lake is the more acidic (alkalinity 15 µeq/L in 1980-81) with measurable decreases in pH and alkalinity occurring since 1979 (Dillon et al. 1987). Harp Lake is less acidic but is still considered acid-sensitive with alkalinity of 61 µeq/L and pH 6.3. Catchment characteristics are listed in Table 1. The lakes are underlain by Precambrian metamorphic silicate bedrock. The Plastic Lake catchment has surficial deposits of thin Pleistocene glacial till (< 1 m) and small areas of peat overlying layers of clay and sand. The Harp Lake catchment has extensive till plains (> 1 m) with some areas of thin till and exposed rock ridges. Smaller deposits of sand and peat (overlying sand) occur. More detailed descriptions of the geology and physiography of the catchments can be found in Jeffries and Snyder (1983), LaZerte and Dillon (1984), Girard et al. (1985), Seip et al. (1985) and Dillon et al. (1987).

The catchments are primarily forested with some cottage development around Harp Lake. Harp Lake has six major tributaries which drain between 10 and 191

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ha of the catchment (Table 1). Plastic Lake has one major inflow and several ephemeral inflows; only the former was treated as a separate subcatchment.

METHODS

The input of NO_3^- and NH_4^+ to the subcatchments from the atmosphere was estimated by measuring bulk deposition rates; methods are described in detail in Dillon et al. (1988).

The output of NO_3^- and NH_4^+ from each of the subcatchments for eight hydrologic years (June 1, 1976 - May 31, 1984) was estimated by combining continuous measurements of stream discharge with instantaneous estimates of substance concentration. Weirs or flumes were installed at the mouth of the seven major inlet streams as well as at the two lake outflows. Discharge was calculated by applying a measured water level-discharge relationship to the continuously-measured stream level (Scheider et al. 1983). Water samples were collected approximately weekly, except during periods of high flow (especially snowmelt), when more samples were taken. Most streams were sampled 35-50 times in any of the 8 years, although the number varied from 28-132. Sample collection techniques were described in detail in Locke and Scott (1986), while analytical methods are outlined in Ontario Ministry of the Environment (1983). Total inorganic nitrogen (TIN) was calculated as NO_3^- plus NH_4^+.

The NO_3^- and NH_4^+ outputs from the lakes were measured in an identical manner. The total inputs to each of the lakes were calculated as the sum of the input(s) from the subcatchments, the input from the ungauged portion of the catchment (prorated on an areal basis) and the atmospheric deposition directly on the lakes' surfaces. Retention in the lake was calculated as the difference between total inputs and output divided by total input.

Budgets for the combined lake-catchment systems were calculated from atmospheric deposition to the total land and water area and output via the lakes' outflows.

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RESULTS

Annual NH_4^+ and NO_3^- input/output data for Canadian catchments and lakes are presented in Table 2. The retentions of NO_3^- (R_{NO_3}), NH_4^+ (R_{NH_4}) and TIN (R_{TIN}) in the Harp and Plastic Lake subcatchments, lakes and lake/catchment systems are shown in Table 3. Since there was, with only one exception, very little difference between years in retention of any of the three parameters as evidenced by the small coefficients of variation ($<$ 10% in most cases), only mean annual values are reported.

A minimum of 94% ($\pm$ 3%) of the NH_4^+ deposited on the subcatchments was retained. The retention of NO_3^- was lower (0.52 - 0.98), although for 37 of 53 catchment-years, it was $>$ 0.8. The lowest figure (0.52 $\pm$ 0.35, Harp 3A) was affected by a single year when R_{NO_3} was -0.05. In that year (1977-78), NO_3^- export from the Harp 3A was greater than precipitation input (i.e. R_{NO_3} $<$ 0) whereas R_{NO_3} was 0.93 in 1976/77. Excluding this value, the mean for Harp 3A was 0.60 $\pm$ 0.29, which was still the lowest average for any subcatchment. The retention of TIN ranged from 0.70 ($\pm$ 0.20) to 0.98 ($\pm$ 0.07), with the lowest value again influenced by the one year's results for Harp 3A.

Retention of both nitrogen species was lower in the two lakes than in the subcatchments of the lakes; i.e. the lakes were less efficient NO_3^- and NH_4^+ sinks. When each lake and its catchment were considered as a whole, they were both extremely effective NH_4^+ sinks (0.98 and 0.95 for Harp and Plastic). The Plastic system was equally effective in retaining NO_3^- (R_{NO_3} = 0.95), while the Harp system was less so (R_{NO_3} = 0.79).

DISCUSSION

The NO_3^- and NH_4^+ budgets of the study lakes and catchments were compared to those reported in the literature. Budgets for several Canadian forested stream catchments and lakes are summarized in Tables 2-4 while Scandinavian and northeastern United States data are summarized in Table 5. For catchment budgets, precipitation was considered to be the only input. Outputs were expressed per m² of catchment, including lake surface where appropriate. For lake budgets, precipitation to the lake surface, stream inlet loads and estimates of direct non-channelized inputs were included and inputs and outputs were expressed per m² of lake surface. Precipitation samples were obtained with bulk collectors in Ontario and with wet-only event samplers at Lac Laflamme, Quebec and Kejimkujik Lake, Nova Scotia. The Kejimkujik data were presented as estimated wet + dry deposition by Kerekes et al. (1982) but only wet deposition is used here.

A.   Catchment Retention

R_{NH_4} for stream catchments and lake/catchment systems in Europe and North America including Harp and Plastic was high ranging from 0.81 - 0.99 for loadings up to 40 meq m⁻² yr⁻¹ except for Jamieson Creek in British Columbia (Table 4).

Mean annual R_{NO_3} for stream catchments reported in Tables 3-5 ranged from 0.15 for Hubbard Brook, New Hampshire to 0.98 in Harp 6A for loadings up to 83 meq m⁻² yr⁻¹. R_{NO_3} was < 0 at Hubbard Brook during 3 of the 11 years (Likens et al. 1977) which indicates conditions promoting nitrification.

Relatively low R_{NO_3} occurred in the Lac Laflamme, Batchawana South and Turkey Lakes catchments and certain Harp Lake subcatchments during some years. Batchawana South and Turkey Lakes have short residence times and rapidly flushing lakes upstream which probably resulted in the low total catchment R_{NO_3} as discussed in the next section.

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Lohi Lake also has a short residence time and an upstream lake. The upstream lake, Clearwater, has a relatively long residence time (3.7 yr) and as a result retains most of its NO_3^-.

Grennfelt and Hultberg (1986) reported that R_{NO_3} was < 0 in several forested catchments in Denmark, Belgium and Czechoslovakia when both high NH_4^+ (54 - 90 meq m^{-2} yr^{-1}) and high NO_3^- deposition (39 - 79 meq m^{-2} yr^{-1}) occurred. R_{NH_4} was high over the entire range of loadings (2.5 - 106 meq m^{-2} yr^{-1}) but at the highest NH_4^+ deposition rate, a relatively high R_{NO_3} of 0.79 occurred. High NH_4^+ deposition may promote low R_{NO_3} by inhibiting NO_3^- assimilation and enhancing nitrification.

In Turkey Lakes Subcatchment 31, annual fluxes of NH_4^+ and NO_3^- from the forest floor to the rooting zone were greater than precipitation inputs (Foster et al. 1986). NH_4^+ was effectively retained within the rooting zone whereas NO_3^- retention occurred primarily below the rooting zone. Significant N_2 fixation or mineralization, and significant nitrification apparently occurred within the forest floor and rooting zone.

Approximately 75% of the total N input to a North Carolina forest (Todd et al. 1975), 69% of the total N input to Hubbard Brook (Likens et al. 1977) and 75% of the total N input to a tundra catchment (Barsdate and Alexander 1975) was fixed N_2. This suggests that atmospheric deposition would have to increase greatly before N saturation occurred if N_2 fixation is a significant N source in unfertilized forested catchments. Forest soils are also a major source of N during forest growth (Fahey 1983; Fahey and Knight 1984; Fahey et al. 1985).

NH_4^+ adsorption by soils is typically high whereas NO_3^- is mobile and in comparision is readily leached (Szperlinski and Badowska 1977a, 1977b). NH_4^+ exported from large agricultural catchments in southern Ontario was highly correlated with suspended solids, unlike NO_3^- (Coote et al. 1982). NO_3^- mobility implies that stream discharge

exerts some control over export and, hence, retention. It appears that NO_3^- is typically the dominant inorganic N species exported from agricultural catchments, regardless of N source, because of microbial transformations. Klein et al. (1983) reported high rates of NO_3^- formation in acid forest soils. Although autotrophic nitrification is inhibited by low pH, heterotrophic nitrification is not (Lang and Jagnow 1986). It follows, therefore, that NO_3^- exported from forested catchments is not necessarily derived from atmospheric NO_3^- and that retention of total inorganic N, R_{TIN}, may be a better indicator of catchment behaviour than retention of the component species.

Knowles (1982) reported terrestrial N_2O flux rates from soils of 4-55 meq m^{-2} yr^{-1} for unfertilized grasslands and parklands, assuming an active microbial community for 180 days yr^{-1}. These rates are comparable to the deposition rates reported here. The optimum pH range for denitrification is 7-8 (Knowles 1982). Hence, terrestrial denitrification rates may be affected by acidification of soils.

R_{TIN} differed between adjacent Harp stream catchments, although TIN deposition was identical, and R_{TIN} did not appear to be a function of wet deposition (Figure 2). Plotting R_{TIN} for Harp, Lake 239 and British Columbia stream catchments as a function of discharge suggests that discharge is an important driving function (Figure 3). The occurrence of high wet deposition at a given site implies that high precipitation and discharge are occurring relative to drier years; hence, both deposition and discharge may appear related to retention. However, plotting Ontario and British Columbia data together emphasizes the role of discharge (Figures 3 and 4) because in British Columbia, extremely high discharge and low wet deposition, relative to Ontario, occurred (Zeman 1975).

Statistical analysis of the relationships between hydrologic phenomena and chemical mass balances is complicated by potential spurious self-correlation (Kenney 1982). Although analysis of the relationships between R and discharge and areal deposition is intuitively satisfying

(Figures 3 and 4), the latter are component variables in the calculation of R.

This is seen in the following,

$$R = 1 - \frac{\Sigma[N]_0}{A_d \; \Sigma[N]_{ppt}} \; \frac{q_0}{PPT} \tag{1}$$

Annual areal wet TIN deposition = $\Sigma[N]_{ppt}$ PPT

Stream discharge = q_0

Where $[N]_{ppt}$ is the TIN concentration in precipitation, PPT is precipitation depth, $[N]_0$ is the TIN concentration in stream discharge and A_d is catchment area.

One clue as to whether the relationships plotted in Figures 3 and 4 are mathematical artifacts is the behaviour of Jamieson Creek in British Columbia (Zeman 1975) which has high precipitation, low deposition, high discharge and very low R (0.20). In areas of high precipitation $q_0 \rightarrow$ PPT and, according to equation (1), R may approach 0. Hence, we can postulate hydrological control of R in a wet temperate forested catchment such as Jamieson Creek.

B.   Lake Retention

Ontario lake retention data are summarized in Table 6.

The NO_3^- retention model of Kelly et al. (1987) relates lake retention, R_{NO_3}, to lake mean depth, $\bar{z}$, and water residence time, τ:

$$R_{NO_3} = \frac{S_{NO_3}}{\bar{z}/\tau + S_{NO_3}} \qquad (2)$$

where S_{NO_3} is a mass transfer coefficient ($m\ yr^{-1}$) and is considered to be a constant for lakes with measurable NO_3^-.

Eq. 2 can be transformed into a linear relationship:

$$\frac{1}{R_{NO_3}} = \frac{1}{S_{NO_3}} \cdot \frac{\bar{z}}{\tau} + 1 \qquad (3)$$

The transformed mean data are highly correlated ($r^2 = 0.90$) and are plotted in Figure 5a. S_{NO_3}, calculated as the reciprocal of the slope (± 95% confidence limits) was 4.83 ± 2.55. Agreement is good except for Batchawana South and Dart's Lakes which have very short and probably highly variable τ (Table 6). Hence, $\bar{z}/\tau$ appears to control R_{NO_3}, at least within the range of NO_3^- loadings (9 - 321 meq m^{-2} lake surface yr^{-1} for the Ontario lakes) and lake pH values observed. R_{NO_3} is probably not affected by lake acidification because denitrification, which may be a major NO_3^- sink, occurs in circum-neutral sediments buffered by anaerobic microbial activity (Stumm and Morgan 1981; Kelly and Rudd 1984; Rudd et al. 1986; Schiff and Anderson 1986).

Rudd et al. (1988) reported that nitrification ceased in two experimentally acidified lakes (Lakes 223 and 302S) at pH 5.4-5.7. Lower NO_3^- concentrations probably contributed to lower NO_3^- export and, hence, to the high R_{NO_3} observed for these lakes. However, NO_3^- accumulations have been observed in acidified Bowland, Lohi and Clearwater Lakes in Ontario (Yan and Dillon 1984; Molot et al. 1989).

Since R_{NO_3} increases with decreasing $\bar{z}/\tau$, smaller retention by lakes compared to stream catchments (Tables 3-6) reflects less contact between NH_4^+ and NO_3^- and microbial communities responsible for consumption in lakes (Keeney et al. 1971; Knowles and Lean 1987). S_{NO_3} was calculated by Kelly et al. (1987) to be 9.2 ± 2.6 (± SD) m yr^{-1} using mass balance data and 7.4 ± 2.6 m yr^{-1} using N-15 denitrification measurements. Variability of S_{NO_3} may reflect in situ variability in turbulence, and microbial denitrification, nitrification and assimilation rates.

Lake retention of NH_4^+ also appeared to be influenced by $\bar{z}/\tau$ (Figure 5b) with r^2 = 0.91 and S_{NH_4} ± 95% confidence limits = 5.6 ± 4.8 for $1/R_{NH_4}$ versus $\bar{z}/\tau$ (Table 4). Correlation was best for $1/R_{TIN}$ versus $\bar{z}/\tau$ with r^2 = 0.92 and S_{TIN} ± 95% confidence limits = 4.4 ± 3.1 (Figure 5c).

Potential for spurious self-correlation also exists in analysis of N retention in lakes. This is seen in Table 7. Good correlation exists between R_{TIN} and some variables which are component variables of R_{TIN} but low correlation exists between R_{TIN} and variables such as mean depth or catchment area which are not component variables. The correlation between R_{TIN} and τ is almost as good as with $\bar{z}/\tau$, although there are theoretical reasons for using the ratio (Kelley et al. 1987). Catchment area is poorly correlated with R_{TIN} although it is an indicator of flushing rate.

The importance of self-correlation can be gauged by comparison with correlations from a randomly generated data set. In this exercise, the data set consisted of 100 lake-years of observations of N concentrations in an inflow stream, the lake outflow and precipitation, discharge from the inflow stream and outflow, precipitation depth, lake surface area and mean depth. The simulated variables were normally distributed using realistic scales. The resulting correlation coefficient between $1/R$ and $\bar{z}/\tau$ was 0.03, and the linear regression r^2 was 0.001. The subset of data with R > 0 and lake

outflow < (stream inflow + precipitation) yielded a correlation coefficient of 0.10. Hence, we can conclude that spurious self-correlation was not significant in this relationship and that $\bar{z}/\tau$ exerts a real and significant effect on N retention in lakes.

C. Effect of NO_3^- and NH_4^+ Consumption on Acidification

The net effect of NH_4^+ and NO_3^- consumption on acidification of lakes is indicated by the ratio of their net consumption in lakes. This assumes that retained NH_4^+ is not adsorbed. If the ratio of consumed NH_4^+ to consumed NO_3^- is > 1, then acidification occurs. As can be seen from the data in Table 8, net N consumption-based acidification was infrequent, occurring in 11 of 42 lake-years.

Furthermore, mean net N consumption-based acidification was highly negatively correlated with $\bar{z}/\tau$ (r^2 = 0.77, Figure 6) and was more likely to occur in lakes with long residence times (i.e. when $\bar{z}/\tau$ is < 1.5 m yr^{-1}). Use of the regression equation in Figure 6 is constrained by the assumption that NH_4^+ and NO_3^- loadings are not independent, although the large ranges for net N consumption-based acidification within a lake suggest otherwise.

Net N consumption-based acidification of soils occurred in the catchments of Turkey Lake, Harp 3A, 3, and 6, Lake 239 and Lake 223 (Table 9). Extremely high levels of NH_4^+ deposition and high nitrification rates in the Netherlands have resulted in pronounced soil acidification (van Breemen et al. 1982).

Although site-specific changes in loading will not alter the proportions retained and exported, at least within the range of loadings for the types of systems reported here, changes in loading will result in changes in the absolute amounts of inorganic N retained and exported. Hence, increased NO_3^- deposition will result in higher NO_3^- concentrations and greater acidity in stream and lake waters, and decreased deposition should result in increased alkalinities. An exception to this may be those systems that are N-limited

and where additional NO_3^- deposition will be consumed. Systems with high areal water discharge rates appear most susceptible to changes in deposition.

CONCLUSIONS

Retention of NO_3^- and NH_4^+ by oligotrophic lakes and forested stream catchments is controlled by local interactions of basin characteristics and hydrology, specifically, areal water discharge rates. Site-specific changes in loading will not alter the proportions retained and exported, at least within the range of loadings for the systems reported here.

However, changes in loading will result in changes in the absolute amounts of inorganic N retained and exported. Hence, increased NO_3^- deposition will result in higher NO_3^- concentrations and greater acidity generation in catchments and lake waters. Decreased deposition should result in increased alkalinities. Systems with high areal water discharge rates appear most susceptible to changes in deposition.

Section II. Changes in Ionic Composition of Streamwater During Snowmelt in
            Central Ontario

INTRODUCTION

Spring depressions of pH and alkalinity in streams and lakes are well-
documented over both a broad geographical scale and over a wide range of
alkalinity (Gjessing et al. 1976; Henriksen and Wright 1977; Hultberg 1977;
Jeffries et al. 1979; Galloway et al. 1980, 1987; Bjarnborg 1983; Keller 1983;
Sharpe et al. 1984; Gunn and Keller 1984, 1986; Jacks et al. 1986; Baird et
al. 1987; Stoddard 1987).   These episodic depressions are caused by base
cation dilution (Galloway et al. 1980b, 1987; Jacks et al. 1986; Stoddard
1987) and/or acid anion increases (Galloway et al. 1980b, 1987; Galloway and
Dillon 1983; LaZerte and Dillon 1984).   This follows from the secondary (or
charge balance) definition of alkalinity:

$$Alk = Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ - SO_4^{2-} - NO_3^- - A^- - Cl^- \quad (4)$$

where A^- represents organic acid anions ($\mu eq\ L^{-1}$) and aluminum species are
excluded because they generally contribute little to the total charge
balance.

The contribution of base cations to alkalinity may be overestimated when
organic acid-cation complexation occurs because the proportion of complexed
cations cannot be determined.

There is some concern that anions such as SO_4^{2-} and NO_3^- dominate alkalinity
depressions in areas of high acid deposition because anions accumulated during
the winter in the snowpack are released during a relatively brief melt period
(Johannessen et al. 1977; Cadle et al. 1984; English et al. 1986; Stottlemyer
1987) when biological activity in the soil and the stream-bottom is low.
Biologically-mediated reduction of these anions consumes acidity (Brewer and
Goldman 1976; Schindler et al. 1985).

The quantitative contribution of anions and cations to alkalinity depressions is complicated by early release of ions from snowpack before maximum discharge is reached (Johannessen et al. 1977; Jacks et al. 1986; Christoperhsen et al. 1984). Anion concentrations in streams may peak well before minimum alkalinities are observed (Jacks et al. 1986), indicating that base cation dilution is at least partially responsible for alkalinity reduction.

This paper presents an analysis of the factors causing short-term (episodic) acidification. The relative contributions of major ions to alkalinity depressions during spring melt in three years (1984-86) are analyzed for 15 headwater streams and lake outflows in three central Ontario watersheds.

STUDY AREA

Harp and Dickie Lakes are located in the District of Muskoka, and Plastic Lake is located in Haliburton County, central Ontario (Figure 1). Plastic Lake is the most acidic (alkalinity approximately 15 μeq L^{-1} in 1980, 5 μeq L^{-1} in 1985) with measurable decreases in pH and alkalinity occurring since 1979 (Dillon et al. 1987). Harp Lake is the least acidic but is still considered acid-sensitive with alkalinity 61 μeq L^{-1} and pH 6.3 in 1985. Catchment characteristics are listed in Table 1 and Harp and Plastic lakes are described in Section I.

The lakes are underlain by Precambrian metamorphic silicate bedrock. The Dickie Lake catchment consists primarily of thin till and exposed rock ridges with smaller deposits of till and peat overlying clay or sand. The watersheds are primarily forested with some cottage development around Harp and Dickie Lakes.

METHODS

Water collection (Locke and Scott 1986), analytical techniques (Ontario Ministry of the Environment 1983) and hydrologic methods (Scheider et al. 1983) are described in detail elsewhere. Briefly, weirs or flumes were installed at the mouth of major inlet streams and at lake outlets. Samples were collected as frequently as possible (> 1/week; average of four times per week) during spring melt in 1984, 1985, and 1986, filtered through 76 μm Nitex mesh into appropriate pre-rinsed sample bottles, and placed in temperature-controlled containers to prevent freezing. Samples were routinely analyzed for Gran alkalinity, pH, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and dissolved organic carbon (DOC). Organic acidity (A^-) was calculated as a function of DOC and pH (Oliver et al. 1983; LaZerte and Dillon 1984).

Sample site codes are denoted by HP (Harp), DE (Dickie) and PC (Plastic). Inlet streams are numbered 1-11 and lake outlets are coded as 0, i.e. the outlet from Harp Lake is coded as HP0.

Alkalinity decreases were delineated by visual inspection of alkalinity versus time plots. A total of 38 episodes were defined by inspection of 43 stream-years of data. Subsequently, daily changes in alkalinity, SO_4^{2-}, NO_3^-, A^- and C_b (Ca^{2+} + Mg^{2+} + Na^+ + K^+) were calculated as the difference between the daily value during an episode and a pre-episode value. The pre-episode value was usually the discrete value immediately prior to the episode. However, in 1984, pre-episode values were relatively constant for an extended period of time, and mean pre-episode values calculated over a one-month period were used for DE0, DE10, PC0, PC1, HP4, HP5 and the first of multiple episodes for HP0, HP3A and HP6. Ion-specific maximum daily relative contributions to alkalinity increases and decreases during alkalinity depressions (df_i) were then calculated as $\Delta SO_4^{2-}/\Delta alk$, $\Delta NO_3^-/\Delta alk$, $\Delta C_b/\Delta alk$, and $\Delta A^-/\Delta alk$ where:

$$\Delta alk = \text{alkalinity (day 0)} - \text{alkalinity (day i)} \qquad (5)$$
$$\Delta C_b = C_b \text{ (day 0)} - C_b \text{ (day i)} \qquad (6)$$

$$\Delta SO_4^{2-} \quad = SO_4^{2-} \text{ (day i)} - SO_4^{2-} \text{ (day 0)} \tag{7}$$

$$\Delta NO_3^{-} \quad = NO_3^{-} \text{ (day i)} - NO_3^{-} \text{ (day 0)} \tag{8}$$

$$\Delta A^{-} \quad\quad = A^{-} \text{ (day i)} - A^{-} \text{ (day 0)} \tag{9}$$

The magnitude of the alkalinity change, Δalk, is the result of the net change in ion concentrations. Positive values of df_i denote contributions to alkalinity decreases and negative values denote contributions to alkalinity increases. Positive and negative values may occur simultaneously, for example when both anions and cations are diluted. The theoretical sum of the four contributions on any given day (Σdf_i) is 1, ignoring minor ions.

RESULTS AND DISCUSSION

Seasonal cycles of C_b, SO_4^{2-} and NO_3^{-} concentrations were discernible during the year in the Harp, Plastic and Dickie inflows. Minimum C_b typically occurred during spring melt while minimum SO_4^{2-} (<100 μeq.L^{-1}) occurred during summer months (Figure 7). A maximum C_b of 850 μeq.L^{-1} was observed in HP6 in early March, 1985 although C_b and SO_4^{2-} concentrations typically ranged from 100-500 μeq.L^{-1} during the year.

NO_3^{-} concentrations were much less than C_b and SO_4^{2-} with high values observed during spring melt and low values near the detection limit observed during summer months (Figure 7). A maximum of 110 μeq.L^{-1} was observed in HP5 on February 15, 1984. Increases were typically observed during spring melt and were of short duration in inflows.

Lake outflow chemistry appeared somewhat different from inflow chemistry. The extent of seasonal fluctuations in C_b and SO_4^{2-} were markedly less and NO_3^{-} increases lasted longer in outflows (Figure 8).

Thirty-eight spring melt episodes from 12 inlets and 3 outlets were analyzed for the period 1984-86. In a few sites in some years there were no marked alkalinity decreases during snowmelt. During most episodes, concentration changes in ions which contributed to alkalinity decreases were typically

offset by smaller changes in other ions which contributed to alkalinity increases (Figure 9). For example, in HP5 in 1985 C_b dilution was accompanied by anion dilution (Figures 7, 9). Occasionally, two episodes were observed in a stream during spring melt. Maximum alkalinity decrease, episode duration and number of sampling days per episode are listed in Table 10.

The Σdf_i values for all streams and years for Plastic and Harp Lakes (Table 11) ranged from 0.68 to 0.81, which is close to the theoretical value of 1. The value for Dickie Lake was -0.10, suggesting that A^- was overestimated. A^- did not contribute to alkalinity depressions in Dickie Lake inflows despite high A^- concentrations. Depressions in these streams were characterized by dilution of A^-.

An alternate definition of alkalinity was given in equation (4). If alkalinity calculated by the charge balance method were used instead of the measured (by titration) alkalinity, the Σdf_i would be closer to 1 for several reasons. The effects of the minor components of the charge balance (e.g. Al species) would be excluded. In addition, there is a difference between the alkalinity measured by titration and that calculated from pH and DIC measurements attributable to non-linear response of organic ions during the Gran titration. This difference is generally 10-25% (P. Dillon and B. LaZerte unpub. studies), and would be excluded if equation (4) were used for alkalinity.

The major contributor to alkalinity depressions was C_b dilution (i.e. the largest positive df_i numbers in Table 11) although the contribution of C_b dilution in Dickie streams may have been overestimated because of high DOC concentrations.

In general, during the melt periods of 1984 to 1986, NO_3^- increases contributed to alkalinity depressions to a much smaller extent than C_b dilution (Table 11). The larger of the NO_3^- contributions occurred in HPO (first episode), HP3A, HP5, PCO and DEO in 1984 and HPO in 1985 (Table 11).

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The only alkalinity depression dominated by NO_3^- increases occurred in DE0 in 1984, and these increases occurred primarily in the first two weeks of the seven week-long depression. NO_3^- typically contributed to depressions early in episodes in inflow streams but was more evenly distributed over time during depressions in lake outflows.

Alkalinity depressions dominated by SO_4^{2-} contributions were observed in HP0 (first episode), PC0, DE0 and DE5 (both episodes) in 1984, PC1 (first episode) and DE6 in 1985, and HP6A, PC1 (both episodes), DE5, DE6 (both episodes) and DE10 in 1986. These SO_4^{2-} contributions were accompanied by either C_b dilution or increases.

Depressions were more likely to be dominated by anion increases as the degree of acidification increased whereas cation dilution was more likely to dominate depressions in circumneutral systems. SO_4^{2-}-dominated depressions occurred proportionately more often in the more acidic Plastic and Dickie catchments than in the Harp catchment (86% of the 14 SO_4^{2-}- dominated depressions occurred in Plastic and Dickie streams although only 53% of the episodes were in these two catchments). In the outflows of three Adirondack lakes covering a range of acidic conditions (pH 5-7), during spring melt in 1978-80 cation dilution was much larger than the anion increase in more alkaline Panther Lake (pH 7) whereas in acidic Woods Lake (pH 5), C_b dilution was much smaller (Galloway et al. 1980b, 1987). The dominant anion was primarily NO_3^-, unlike central Ontario. Higher NO_3^- concentrations in Adirondack streams may result from differences in forest types or higher areal water discharge rates (Dillon and Molot 1989). Intermediate Sagamore Lake (pH 6) exhibited cation and SO_4^{2-} dilution and a NO_3^- increase. Cation dilution also dominated events in relatively well buffered Djursvasslan stream in Sweden (Jacks et al. 1986) and Gem Lake in California (Stoddard 1987).

The replacement of cation dilution by anion increases as the mechanism responsible for alkalinity depressions in more acidified systems may result in part from depleted terrestrial cation pools or a decrease in weathering rates (Dillon et al. 1987), although cation export may initially increase with the onset of high acid deposition (Likens et al. 1977; Singh et al. 1980). In

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Plastic Lake cation export decreased as acidification increased (Dillon et al. 1987). Hence, prediction of the long-term effect of reductions in SO_4^{2-} deposition on alkalinity depressions must consider the interaction between terrestrial cation pools and SO_4^{2-} (Johnson 1980).

Rustad et al. (1986) applied the 'Birkenes' hydrochemical model to HP4 for the period 1977-82 and predicted that cation dilution (represented by Ca^{2+} and Mg^{2+}) was accompanied by either constant SO_4^{2-} or relatively small SO_4^{2-} decreases during spring melt. This is consistent with observations that cation dilution was primarily responsible for alkalinity depressions in HP4 during spring melt in 1984-86 although small SO_4^{2-} increases were occasionally observed.

Log alkalinity in HP4 (pH > 5.5) was highly correlated with log stream discharge in 1984 (r^2 = 0.73) and discharge episodes coincided closely with alkalinity depressions (Figures 10 and 11). Dilution of cations in HP4 in 1977-82 was strongly coupled to peak discharge (Rustad et al. 1986). pH was also highly negatively correlated with discharge over a 12 month period within each of four Pennsylvania streams (Sharpe et al. 1984). Baseflow pH was greater than 5.0 in the four streams. Maximum changes in H^+ and alkalinity in a circumneutral Pennsylvania stream during storm events during the growing season were best predicted by multiple linear regressions of hydrological parameters (Lynch et al. 1986).

In very acidic PC1 (pH < 4.5), however, log |alkalinity| (all alkalinities were negative) was poorly correlated with log discharge in 1984 (r^2 = 0.23) (Figure 11) and the major discharge events (B and C) on April 5 and April 19 produced only minor alkalinity depressions (Figure 12). (The log-log correlation showed a slight dependence on the mathematical transformation of the alkalinity argument, with r^2 for log (alkalinity +70) and log (alkalinity +200) versus log discharge being 0.15 and 0.20, respectively.) The alkalinity episode of February 14 to March 19, 1984, which coincided with discharge event A, was due primarily to C_b dilution (Figure 13) with some anion dilution occurring (Table 11). During the April discharge events B and C, (Figure 12), dilution of SO_4^{2-} and C_b was considerably smaller resulting in smaller

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dilution of SO_4^{2-} and C_b was considerably smaller resulting in smaller alkalinity changes (i.e. runoff was similar in composition to stream water). Hence, discharge may be a poor predictor of alkalinity depressions in very acidic streams which is consistent with observations that SO_4^{2-} increases are important during depressions in these streams.

Plots of relative daily contributions to alkalinity depressions for the other 37 episodes are shown in Figures 14 to 50. Daily stream chemistry for the 15 streams and lake outflows are shown in Figures 51 to 90.

CONCLUSIONS

1. Alkalinity depressions occurred in streams over a wide range of background alkalinity.

2. Alkalinity depressions were more likely to be dominated by SO_4^{2-} increases as the degree of stream acidification increased. C_b dilution dominated depressions in circum-neutral streams. SO_4^{2-} concentrations were typically much higher than NO_3^- concentrations in the central Ontario streams. Hence, episodic alkalinity depressions are not necessarily precursors to chronic acidification.

3. Organic acidity (A^-) did not contribute to alkalinity depressions in Dickie Lake streams despite high A^-. Depressions in these streams were characterized by dilution of A^-.

4. Discharge was a good predictor of alkalinity in circum-neutral streams but not in an acidic stream. A hydrobiogeochemical model, such as a modified 'Birkenes' model, is necessary for prediction of acidic stream chemistry.

5. Lake outflow chemistry appeared different from inflow chemistry in central Ontario, primarily in the extent of seasonal fluctuations.

ACKNOWLEDGEMENTS

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Table 1. Catchment characteristics of study sites.

			Area (ha)	Bedrock Geology[a]	Surficial Geology[b]
Harp	Inflow	3	26.0	1	10
	Inflow	3A	19.7	1 , 3	10
	Inflow	4	119.6	3	10, 7, 8
	Inflow	5	190.5	1	10, 7, 6, 8
	Inflow	6	10.0	2, 1	7, 10
	Inflow	6A	15.3	1	7
	Outflow	0	542.5[c]	–	–
Plastic	Inflow	1	23.3	4	7
	Outflow	0	127.6[c]	–	–
Dickie	Inflow	5	30.0	5	7, 9
	Inflow	6	21.8	5	7, 9
	Inflow	8	67.0	5	7, 10, 9
	Inflow	10	78.9	5	7, 9
	Inflow	11	76.3	5	7, 9
	Outflow	0	500.4[c]	–	–

[a]   1 Granitized biotite and horneblende gneiss,
        2 Diorite, 3 Amphibolite and schist, 4 Ortho-gneiss,
        5 Horneblende migmatite.

[b]   6 Peat over sand, 7 Thin till and rock ridges, 8 Sand
        9 Peat over clay over sand, 10 Minor till plain.

[c]   Includes lake area plus ungauged inflowing tributaries.

Table 2. Annual NH$_4^+$ and NO$_3^-$ (meq/m²/yr) inputs and outputs for several Canadian lakes and watersheds. Areal units are per m² of watersheds (or per m² of lake surface for lake budgets). Inputs are precipitation for watersheds, and precipitation and drainage for lakes.

| | NH$_4^+$ | | NO$_3^-$ | |
	In	Out	In	Out
Harp Lake				
		1976/77		
Inlet 3	24.22	0.58	38.13	2.13
3A	24.22	0.22	38.13	2.65
4	24.22	1.68	38.13	1.35
5	24.22	2.36	38.13	1.84
6	24.22	0.71	38.13	3.61
6A	24.22	0.29	38.13	0.51
Lake	35.02	3.37	50.03	16.21
Watershed + Lake	24.22	0.44	38.13	2.13
		1977/78		
Inlet 3	33.02	1.85	47.23	13.40
3A	33.02	1.02	47.23	49.80
4	33.02	3.17	47.23	5.15
5	33.02	1.63	47.23	3.82
6	33.02	1.62	47.23	17.70
6A	33.02	0.65	47.23	2.60
Lake	46.03	9.06	107.07	25.72
Watershed + Lake	33.02	1.19	47.23	3.39
		1978/79		
Inlet 3	39.23	0.99	42.73	4.40
3A	39.23	1.18	42.73	11.78
4	39.23	2.15	42.73	4.88
5	39.23	1.77	42.73	3.75
6	39.23	3.22	42.73	10.25
6A	39.23	0.83	42.73	1.06
Lake	50.93	11.41	75.05	48.03
Watershed + Lake	39.23	1.51	42.73	6.32
		1979/80		
Inlet 3	30.22	2.10	47.53	5.25
3A	30.22	0.68	47.53	8.51
4	30.22	1.27	47.53	4.72
5	30.22	1.91	47.53	5.74
6	30.22	1.36	47.53	9.46
6A	30.22	0.61	47.53	1.21
Lake	40.33	6.83	83.86	46.73
Watershed + Lake	30.22	0.90	47.53	6.15

Table 2. (Cont'd)

| | NH$_4^+$ | | NO$_3^-$ | |
	In	Out	In	Out
Harp Lake				
			1980/81	
Inlet 3	32.42	1.60	42.43	16.29
3A	32.42	0.61	42.43	37.44
4	32.42	1.87	42.43	5.09
5	32.42	1.32	42.43	5.66
6	32.42	1.72	42.43	10.82
6A	32.42	0.41	42.43	1.59
Lake	41.73	4.00	100.07	38.73
Watershed + Lake	32.42	0.53	42.43	5.10
			1981/82	
Inlet 3	26.52	0.52	42.63	16.90
3A	26.52	0.31	42.63	30.06
4	26.52	2.60	42.63	4.89
5	26.52	0.92	42.63	7.20
6	26.52	1.09	42.63	11.82
6A	26.52	0.11	42.63	0.91
Lake	35.02	2.64	101.07	43.13
Watershed + Lake	26.52	0.34	42.63	5.68
			1982/83	
Inlet 3	25.82	0.45	36.93	7.00
3A	25.82	0.11	36.93	14.29
4	25.82	1.15	36.93	3.48
5	25.82	0.90	36.93	4.80
6	25.82	1.11	36.93	10.96
6A	25.82	0.06	36.93	0.38
Lake	31.32	1.69	72.25	35.62
Watershed + Lake	25.82	0.22	36.93	4.69
			1983/84	
Inlet 3	22.52	0.13	36.83	5.00
3A	22.52	0.11	36.83	10.94
4	22.52	0.75	36.83	3.03
5	22.52	0.51	36.83	10.27
6	22.52	0.51	36.83	8.96
6A	22.52	0.07	36.83	0.89
Lake	25.72	1.99	83.86	32.02
Watershed + Lake	22.52	0.26	36.83	4.22

Table 2. (Cont'd)

	NH_4^+			NO_3^-	
	In	Out		In	Out
Plastic Lake					
			1979/80		
Inlet 1	30.22	0.78		47.56	1.29
Lake	32.45	11.98		51.34	10.49
Watershed + Lake	30.22	3.02		47.56	2.64
			1980/81		
Inlet 1	32.45	0.38		42.45	0.93
Lake	33.56	7.05		45.34	9.78
Watershed + Lake	32.45	1.77		42.45	2.46
			1981/82		
Inlet 1	26.45	0.20		42.67	1.13
Lake	27.11	4.69		46.00	8.27
Watershed + Lake	26.45	1.18		42.67	2.08
			1982/83		
Inlet 1	25.78	0.14		36.89	0.91
Lake	26.22	3.64		39.56	6.76
Watershed + Lake	25.78	0.92		36.89	1.70
			1983/84		
Inlet 1	22.45	0.09		36.89	1.40
Lake	22.67	3.22		40.89	7.27
Watershed + Lake	22.45	0.81		36.89	1.83

Table 2. (Cont'd)

	NH_4^+			NO_3^-	
	In	Out		In	Out
Lake 239, Ontario					
			_1971_		
NW Inlet	15.27	0.32		40.13	0.33
Lake	17.28	1.61		43.10	3.24
Watershed + Lake	15.27	0.22		40.13	0.45
			_1972_		
NW Inlet	30.93	0.18		19.06	0.31
Lake	32.27	1.11		21.33	3.88
Watershed + Lake	30.93	0.15		19.06	0.54
			_1973_		
NW Inlet	11.76	0.21		11.86	0.20
Lake	13.45	1.60		14.48	2.96
Watershed + Lake	11.76	0.22		11.86	0.41
			_1974_		
NW Inlet	13.86	0.31		13.25	0.32
Lake	17.55	4.09		20.41	7.75
Watershed + Lake	13.86	0.57		13.25	1.07
			_1975_		
NW Inlet	12.12	0.17		14.27	0.20
Lake	14.38	2.17		27.15	4.35
Watershed + Lake	12.12	0.30		14.27	0.60
			_1976_		
NW Inlet	11.69	0.10		9.69	0.14
Lake	13.01	1.29		17.07	5.07
Watershed + Lake	11.69	0.18		9.69	0.70
			_1977_		
NW Inlet	11.14	0.31		13.11	0.77
Lake	14.80	1.10		22.02	2.85
Watershed + Lake	11.14	0.15		13.11	0.40

Table 2. (Cont'd)

	NH_4^+			NO_3^-	
	In	Out		In	Out
Lake 239, Ontario					
			_1978_		
NW Inlet	9.35	0.22		7.41	0.07
Lake	11.27	2.21		9.76	7.84
Watershed + Lake	9.35	0.31		7.41	1.09
			_1979_		
NW Inlet	20.27	0.37		15.38	1.24
Lake	22.83	3.64		23.31	6.50
Watershed + Lake	20.27	0.50		15.38	0.90
			_1980_		
NW Inlet	10.77	0.19		12.69	1.17
Lake	12.46	1.03		18.16	2.35
Watershed + Lake	10.77	0.14		12.69	0.33
			_1981_		
NW Inlet	11.17	0.35		8.41	3.59
Lake	12.88	1.08		21.36	1.54
Watershed + Lake	11.17	0.15		8.41	0.21
			_1982_		
NW Inlet	17.16	0.29		15.20	0.98
Lake	19.50	2.46		23.08	6.78
Watershed + Lake	17.16	0.34		15.20	0.94
			_1983_		
NW Inlet	17.89	0.29		21.94	0.54
Lake	19.62	1.47		24.59	3.52
Watershed + Lake	17.89	0.20		21.94	0.49

Table 2. (Cont'd)

	NH_4^+			NO_3^-	
	In	Out		In	Out
Lake 223, Ontario					
			1976		
Lake	12.23	0.97		10.55	1.49
Watershed + Lake	11.69	0.10		9.69	0.16
			1977		
Lake	13.15	0.57		17.56	0.20
Watershed + Lake	11.14	0.06		13.11	0.02
			1978		
Lake	10.90	2.61		11.77	5.00
Watershed + Lake	9.35	0.27		7.41	0.52
			1979		
Lake	22.70	2.47		22.05	2.49
Watershed + Lake	20.21	0.26		15.38	0.26
			1980		
Lake	11.83	0.76		18.61	0.72
Watershed + Lake	10.77	0.08		12.69	0.08
			1981		
Lake	12.94	0.47		26.25	0.17
Watershed + Lake	11.17	0.05		8.41	0.02
			1982		
Lake	18.74	2.99		20.30	0.78
Watershed + Lake	17.16	0.31		15.20	0.08
			1983		
Lake	19.86	2.36		24.89	0.53
Watershed + Lake	17.89	0.25		21.93	0.06

Table 2. (Cont'd)

	NH$_4^+$			NO$_3^-$	
	In	Out		In	Out
Clearwater Lake, Ontario					
			1977/78		
Inlet 1	29.30	0.88		41.02	1.32
2	29.30	0.89		41.02	2.34
4	29.30	4.46		41.02	1.87
Lake	36.29	8.04		47.74	16.20
Watershed + Lake	29.30	1.47		41.02	2.96
			1978/79		
Inlet 1	22.84	1.05		35.52	1.17
2	22.84	0.58		35.52	0.75
4	22.84	2.61		35.52	1.69
Lake	28.52	8.45		40.90	26.52
Watershed + Lake	22.84	1.54		35.52	4.84
Lohi Lake, Ontario					
			1977/78		
Lake	46.61	18.99		74.73	24.85
Watershed + Lake	29.28	1.38		40.99	1.81
			1978/79		
Lake	41.31	24.06		88.27	68.66
Watershed + Lake	22.82	1.75		35.49	4.99

Table 2. (Cont'd)

	NH$_4^+$			NO$_3^-$	
	In	Out		In	Out
Batchawana South, Ontario					
			1981/82		
Lake	58.38	33.53		240.50	167.82
Watershed + Lake	27.30	2.28		39.00	11.41
			1982/83		
Lake	46.71	39.71		185.60	160.17
Watershed + Lake	25.95	2.70		39.00	10.89
Turkey Lake, Ontario					
			1981/82		
Lake	36.55	27.95		321.10	228.86
Watershed + Lake	37.30	1.81		39.00	14.82
			1982/83		
Lake	34.27	19.61		292.29	213.41
Watershed + Lake	25.96	1.27		39.00	13.82
Turkey Lakes Watershed					
			1983		
Basin 31	19.29	2.14		29.29	18.57
Lac Laflamme, Quebec					
1981 Watershed + Lake	12.64	–		20.79	11.36
1982 Watershed + Lake	12.42	–		24.00	7.86
1983 Watershed + Lake	–	–		22.64	7.21
1984 Watershed + Lake	16.21	–		26.14	6.00
Kejimkujik Lake, Nova Scotia					
			1979/80		
Watershed + Lake	4.92	0.94		11.92	0.09

Table 3. Retention of NH_4^+, NO_3^-, and TIN (= NO_3^- + NH_4^+) in study lakes and catchments. Means ± 1 SD are shown. For Harp Lake, n = 8 yr (1976-84); for Plastic, n = 5 (1979-84).

Location	R_{NO_3}	R_{NH_4}	R_{TIN}
Harp Lake, Ontario			
Inlet 3	0.79 ± 0.13	0.97 ± 0.02	0.86 ± 0.08
3A	0.52 ± 0.35	0.99 ± 0.01	0.70 ± 0.20
4	0.91 ± 0.03	0.94 ± 0.03	0.92 ± 0.02
5	0.87 ± 0.07	0.95 ± 0.02	0.90 ± 0.04
6	0.75 ± 0.08	0.96 ± 0.02	0.84 ± 0.05
6A	0.98 ± 0.01	0.99 ± 0.01	0.98 ± 0.01
Lake	0.57 ± 0.13	0.88 ± 0.06	0.67 ± 0.09
Catchment + Lake	0.79 ± 0.29	0.98 ± 0.01	0.92 ± 0.02
Plastic Lake, Ontario			
Inlet 1	0.97 ± 0.01	0.99 ± 0.01	0.98 ± 0.07
Lake	0.81 ± 0.02	0.79 ± 0.10	0.80 ± 0.04
Catchment + Lake	0.95 ± 0.01	0.95 ± 0.03	0.85 ± 0.01

Table 4. Retention of NH_4^+, NO_3^-, and TIN (= NO_3^- + NH_4^+) in Canadian catchments and lake/catchment systems. Numbers are mean ± 1 SD; n is number of years of data.

Location	n	R_{NO_3}	R_{NH_4}	R_{TIN}	Reference
Lake 223, Ontario Catchment + Lake	8 (1976-83)	0.98 ± 0.02	0.99 ± 0.01	0.99 ± 0.02	) Schindler et al.
					) (1976, 1980a, 1980b)
					) Newbury et al. (1980)
Lake 239, Ontario Northwest Subcatchment	13 (1971-83)	0.94 ± 0.11	0.98 ± 0.01	0.96 ± 0.05	) Linsey et al. (1987)
Catchment + Lake		0.95 ± 0.04	0.98 ± 0.01	0.98 ± 0.02	)
Batchawana South, Ontario Mean of 4 Subcatchments	2 (1981-83)	0.63	0.97	0.77	) Jeffries and Semkin
Catchment + Lake		0.72	0.91	0.80	) (1982, 1983)
					) Semkin and Jeffries
Turkey Lake, Ontario Mean of 3 Subcatchments	2 (1981-83)	0.40	0.97	0.63	) (1983)) Jeffries (unpub.
Catchment + Lake		0.63	0.94	0.78	) studies)
					)
Turkey Lakes, Ontario Subcatchment 31	1 (1983)	0.37	0.89	0.57	)
Kejimkujik Lake, Nova Scotia Catchment + Lake	1 (1979-80)	0.99	0.81	0.94	Kerekes et al. (1982)
Lac Laflamme, Quebec Catchment + Lake	4 (1981-84)	0.64	–	–	Papineau (1987)
Lohi Lake, Ontario Catchment + Lake	2 (1977-79)	0.91	0.94	0.92	) Jeffries et al.) (1984)
					) Scheider (1984)
Clearwater Lake, Ontario Subcatchment 1	2 (1977-79)	0.97	0.96	0.97	) Yan and Dillon (1984)
Subcatchment 2		0.96	0.97	0.97	)
Subcatchment 4		0.95	0.87	0.92	)
Catchment + Lake		0.90	0.94	0.92	)
Jamieson Creek, BC Catchment	1 (1970-71)	0.27	0.05	0.20	Zeman (1975)

Table 5. Reported mean annual retention, precipitation inputs and outputs for NH_4^+ and NO_3^- in Scandinavian and northeastern United States systems. tw is total catchment including lake.

System	Years	Input meq/m²/yr	Output meq/m²/yr	R	Reference
NO_3^-					
Bickford Watershed	1981-83				
West Wachusett Brook		29.5	1.0	0.97	Hemond and
Provencial Brook		29.5	0.79	0.97	Eshleman (1984)
Bickford Reservoir		82.5	58.2	0.29	
Hubbard Brook	1963-74	30.7	26.0	0.15	Likens et al. (1977)
Adirondacks	1978-80				
Panther tw		–	–	0.35	Galloway et al.
Sagamore tw		–	–	0.43	(1980)
Woods tw		–	–	0.54	
Birkenes	1972-78	53	8	0.85	Wright and Johannesson (1980)
Langtjern tw	1973-75[1]	27.0	1.05	0.96	Henriksen and Wright (1977)
Langtjern	1974-80				
Subcatchment 2		25.3	1.1	0.96	
Subcatchment 3		25.3	0.9	0.96	
tw		25.3	1.4	0.94	
NH_4^+					
Hubbard Brook	1963-74	16.0	1.9	0.88	Likens et al. (1977)
Adirondacks	1978-80				Galloway et al.
Panther tw		–	–	0.92	(1980)
Sagamore tw		–	–	0.98	
Woods tw		–	–	0.87	
Langtjern tw[1]	1973-75	22.5	–	–	Henriksen and Wright (1977)

[1] Dry deposition estimated using Cl method.

Table 6. Mean Lake NO_3^-, NH_4^+, and TIN retention, water residence time (τ, in yr), mean depth ($\bar{z}$ in m, pH) and mass transfer coefficients (S, in m yr^{-1}) in several Ontario lakes.

Lake	Budget Years	R_{NH_4}	R_{NO_3}	R_{TIN}	τ	$\bar{z}$	S_{NO_3}	S_{NH_4}	S_{TIN}	pH
239	1976-83	0.89	0.73	0.82	6.2	10.9	4.76	14.67	7.97	6.5-6.8
223	1976-83	0.84	0.90	0.90	8.7	7.2	7.47	6.92	7.47	5.0-6.7
Harp	1976-84	0.88	0.57	0.67	2.5	13.3	6.50	48.36	10.80	6.2-6.3
Plastic	1979-84	0.79	0.81	0.80	3.0	8.0	11.38	9.89	10.68	5.7-5.9
Lohi	1977-79	0.51	0.45	0.46	1.0	6.2	5.07	6.33	5.28	4.7-5.3
Clearwater	1977-79	0.74	0.51	0.61	3.7	8.3	2.33	3.03	3.50	4.1-4.5
Batchawana South	1981-83	0.29	0.22	0.24	0.3	3.3	3.10	4.49	3.47	5.9
Turkey	1981-83	0.34	0.28	0.29	0.9	12.2	5.27	6.81	5.54	6.7
Regression estimate using Eq. (±95% confidence limits), n = 8 lakes							4.20 ±3.70	5.59 ±4.84	4.39 ±3.14	
Crystal[1]	1984	–	0.99	–	25.0	10.6	–	–	–	?
302N[1]	1981-84	–	0.70	–	5.8	5.7	2.3	–	–	6.2-6.6
302S[1]	1981-84	–	0.98	–	8.3	5.1	–	–	–	5.6-6.6
Langtjern[1]	1972-78	–	0.36	–	0.20	2.4	6.8	–	–	4.6-4.8
Regression estimate using Eg. 2 (±95 confidence limits), n = 12 lakes							4.83 ±2.55	–	–	

[1] Data from Kelly et al. (1987).

Table 7. Correlation coefficients between lake TIN retention and several variables for eight Ontario lakes.

Variable	r
Area loading = $\Sigma[N]_i\, q_i/A_L + \Sigma[N]_{ppt}\, PPT$	-0.91
Volumetric loading = $(\Sigma[N]_i\, q_i + \Sigma[N]_{ppt}\, PPT\, A_L)/V_L$	-0.80
Flushing rate, $\tau = V_L/\Sigma q_o/A_L$	0.86
$\bar{z}/\tau = \Sigma q_o/A_L$	-0.92
Mean depth, $\bar{z} = V_L/A_L$	0.25
A_d	-0.21
A_L	0.22

$$R = 1 - \frac{\Sigma[N]_o\, q_o}{\Sigma[N]_i\, q_i + \Sigma[N]_{ppt}\, PPT\, A_L}$$

where
R lake TIN retention
$[N]_i$ TIN concentration in inflow streams
$[N]_o$ TIN concentration in outflow stream
$[N]_{ppt}$ TIN concentration in precipitation
q_i stream inflow
q_o stream discharge
PPT precipitation depth
A_L lake area

V_L lake volume
$\bar{z}$ lake mean depth
τ lake flushing rate, $V_L/\Sigma q_o$
A_d catchment area

Table 8. Ratio of NH_4^+ to NO_3^- consumption in several Ontario lakes. Net N consumption-based acidification occurs when the ratio of consumed NH_4^+ to consumed NO_3^- is > 1.

Lake		NH_4^+/NO_3^-	Lake		NH_4^+/NO_3^-
Harp	1976/77	0.94	Lake 223	1976	1.24
	1977/78	0.45		1977	0.72
	1978/79	1.46		1978	1.22
	1979/80	0.90		1979	1.04
	1980/81	0.39		1980	0.62
	1981/82	0.56		1981	0.48
	1982/83	0.81		1982	0.81
	1983/84	0.46		1983	0.72
Mean (±SD)		0.75±0.36	Mean (±SD)		0.86±0.28
Plastic	1979/80	0.50			
	1980/81	0.75			
	1981/82	0.59	Clearwater	1977/78	0.90
	1982/83	0.69		1978/79	1.40
	1983/84	0.58	Mean		1.15
Mean (±SD)		0.62±0.10			
Lake 239	1971	0.39	Lohi	1977/78	0.55
	1972	1.79		1978/79	0.88
	1973	1.03	Mean		0.72
	1974	1.06			
	1975	0.54			
	1976	0.98			
	1977	0.71	Batchawana	1981/82	0.34
	1978	4.72	South	1982/83	0.28
	1979	1.14	Mean		0.31
	1980	0.72			
	1981	0.60			
	1982	1.05			
	1983	0.86	Turkey	1981/82	0.09
Mean (±SD)	1971-83	1.20±1.11		1982/83	0.19
Excluding	1978	0.91±0.37	Mean		0.14

Table 9. Ratio of NH_4^+ to NO_3^- consumption in several Ontario catchments. Net N consumption-based acidification occurs when the ratio is > 1. tw is total catchment including lake.

		1976/77	1977/78	1978/79	1979/80	1980/81	1981/82	1982/83	1983/84	Mean
Harp	3	0.66	0.92	1.00	0.67	1.18	1.01	0.85	0.70	0.87
	3A	0.68	> 1	1.23	0.76	6.37	2.09	1.14	0.87	-
	4	0.61	0.71	0.98	0.68	0.82	0.63	0.74	0.64	0.73
	5	0.60	0.72	0.96	0.68	0.85	0.72	0.78	0.83	0.77
	6	0.68	1.06	1.10	0.76	0.97	0.82	0.95	0.80	0.89
	6A	0.64	0.72	0.92	0.64	0.78	0.63	0.70	0.62	0.71
	tw	0.66	0.73	1.04	0.71	8.62	0.71	0.79	0.68	1.74
Plastic	1				0.64	0.77	0.63	0.71	0.63	0.68
	tw				0.61	0.77	0.62	0.71	0.62	0.67
Clearwater	1		0.72	0.63						0.68
	2		0.73	0.64						0.69
	4		0.63	0.60						0.62
	tw		0.73	0.69						0.71
Lohi	tw		0.71	0.69						0.70
Batchawana South	tw						0.91	0.83		0.87
Turkey	tw						1.05	0.98		1.02
Kejimkujik	tw				0.35					

		1971	1972	1973	1974	1975	1976	1977	1978	1979
Lake 239	NW	0.38	1.64	0.99	1.05	0.85	1.21	0.88	1.24	1.41
	tw	0.38	1.66	1.01	1.09	0.86	1.28	0.86	1.43	1.37

		1980	1981	1982	1983	Mean
	NW	0.85	2.24	1.19	0.82	1.13
	tw	0.86	1.34	1.18	0.82	1.09

		1976	1977	1978	1979	1980	1981	1982	1983	Mean
Lake 223	tw	1.22	0.85	1.32	1.32	0.85	1.33	1.11	0.81	1.10

Table 10. Maximum alkalinity decrease (μeq.L^{-1}) relative to pre-episode value, episode duration and number of days sampled (n) for each alkalinity depression in Harp, Plastic and Dickie streams. The #1 and #2 refer to cases where there were multiple episodes in a single year.

Site	ΔALK $_{max}$	Days	n
1984			
HPO #1	17	32	22
HPO #2	17	21	11
HP3	48	29	21
HP3A	24	24	19
HP4	15	30	22
HP5	47	28	21
HP6 #1	24	22	17
HP6 #2	31	41	22
PCO	10	59	38
PC1	22	34	20
DEO	17	48	28
DE5 #1	51	33	21
DE5 #2	41	41	27
DE6	27	49	27
DE10	6	35	23
DE11	27	33	19
1985			
HPO	27	39	17
HP3	60	68	67
HP4	88	81	74
HP5	59	80	71
HP6	40	81	70
PCO	21	28	9
PC1 #1	31	28	16
PC1 #2	17	44	21
DEO	23	61	24
DE6	32	36	37
1986			
HP3	80	59	37
HP4	111	63	40
HP5	97	63	39
HP6	69	69	39
HP6A	24	46	29
PC1 #1	16	28	9
PC1 #2	77	59	21
DE5	67	42	18
DE6 #1	18	21	10
DE6 #2	20	21	7
DE8	21	39	18
DE10	18	47	21

Table 11. Cumulative daily changes in major ions relative to alkalinity (dimensionless) in stream inflows and lake outflows during alkalinity depressions.

		$\dfrac{\sum \Delta NO_3^-}{\sum \Delta alk}$	$\dfrac{\sum \Delta SO_4^{2-}}{\sum \Delta alk}$	$\dfrac{\sum \Delta A^-}{\sum \Delta alk}$	$\dfrac{\sum \Delta C_b}{\sum \Delta alk}$	$\dfrac{\sum (\Delta NO_3^- + \Delta SO_4^{2-} + \Delta A^- + \Delta C_b)^a}{\sum \Delta alk}$
1984						
HP0	#1	0.96	1.07	0.34	-2.92	-0.55
HP0	#2	-0.21	-1.87	-0.37	3.02	0.58
HP3		0.06	-0.33	-0.14	1.10	0.68
HP3A		0.77	-2.78	0.71	2.04	0.72
HP4		0.11	0.14	0.02	0.66	0.93
HP5		0.63	-0.74	-0.54	1.24	0.60
HP6	#1	0.10	-3.78	0.24	2.18	-1.26
HP6	#2	-0.55	-2.18	0.08	5.79	3.14
PC0		0.65	0.86	0.11	-2.55	-0.94
PC1		-0.39	-1.33	0.07	3.34	1.69
DE0		0.53	0.41	0.30	-2.24	-1.00
DE5	#1	-0.17	0.70	-3.40	1.01	-1.72
DE5	#2	-0.002	0.91	-2.15	1.13	-0.12
DE6		-1.55	0.09	0.16	8.38	7.08
DE10		0.85	-22.81	-6.10	26.89	-1.16
DE11		-0.24	-1.42	-0.01	2.59	0.92
1985						
HP0		0.41	0.28	-0.16	1.00	1.53
HP3		-0.09	-0.38	-0.31	1.94	1.16
HP4		-0.01	-0.32	-0.03	1.33	0.97
HP5		0.07	-0.09	-0.56	1.36	0.78
HP6		0.10	-1.35	0.002	0.40	-0.85
PC0		-0.23	-0.37	0.08	2.08	1.57
PC1	#1	-0.18	1.38	-0.66	0.45	1.00
PC1	#2	-0.10	-1.26	-0.77	2.74	0.61
DE0		0.20	-0.32	-0.08	0.90	0.70
DE6		0.03	1.84	-0.85	-0.60	0.42
1986						
HP3		-0.05	-0.27	0.03	0.99	0.70
HP4		-0.05	-0.06	-0.08	1.21	1.02
HP5		0.004	0.19	-0.23	0.87	0.83
HP6		0.11	-0.91	-0.01	0.57	-0.25
HP6A		0.10	0.45	-1.06	1.96	1.45
PC1	#1	-0.14	1.46	-0.73	-1.05	-0.45
PC1	#2	-0.27	1.48	-0.97	1.33	1.57
DE5		0.02	0.81	-1.04	0.50	0.28
DE6	#1	0.03	1.21	-1.11	-1.32	-1.20
DE6	#2	0.13	3.75	-4.16	-2.02	-2.30
DE8		0.08	-0.48	-4.12	1.02	-3.50
DE10		-0.05	3.70	-4.63	1.24	0.25
1984-86 (Mean ± SD)						
HARP		0.14±0.36	-0.72±1.24	-0.11±0.38	1.37±1.63	0.68±0.98
HARP w/o HP6[b]		0.19±0.36	-0.34±0.97	-0.17±0.42	1.13±1.32	0.81±0.49
PLASTIC		-0.09±0.34	0.32±1.28	-0.41±0.47	0.91±2.11	0.72±1.05
DICKIE		-0.01±0.54	-0.89±6.75	-2.09±2.15	2.88±7.69	-0.10±2.52

[a] Theoretical value of $\sum df_i$ is 1.
[b] HP6 excluded because of road salt inputs.

FIGURES

Figure 1.   Location of the study lakes and their subcatchments.

Figure 2.   Annual wet ¯deposition and TIN retention (R_{TIN}) for Harp
             stream catchments.

Figure 3.   Annual stream catchment R_{TIN} versus water discharge for Harp
             (3, 3A, 4, 5, 6, 6A), Lake 239 (Northwest) and Jamieson Creek,
             British Columbia.

Figure 4.   Annual stream catchment R_{TIN} versus TIN deposition for Harp
             (3, 3A, 4, 5, 6, 6A), Lake 223 (Northwest) and Jamieson Creek,
             British Columbia.

Figure 5.   Reciprocal of mean lake (a) NO_3^-, (b) NH_4^+ and (c) TIN retention
             versus $\bar{z}/\tau$ using data from Table 5. The line was fit with
             ordinary least squares regression. Error bars are ranges.

Figure 6.   Ratio of mean consumed NH_4^+ to mean consumed NO_3^- in lakes
             versus $\bar{z}/\tau$. Acidification occurs when the ratio is > 1.
             The line was fit with ordinary least squares regression using data
             from   Table 6. Error bars indicate ranges.

Figure 7.   Daily alkalinity, NO_3^-, C_b, SO_4^{2-} and A^- in Harp 5 in 1985.

Figure 8.   Daily alkalinity, NO_3^-, C_b, SO_4^{2-} and A^- in Harp outflow in
             1984.

Figure 9.   Relative daily contributions of changes in C_b, SO_4^{2-}, NO_3^- and
             A^- to alkalinity depressions (df_i) in HP5 in 1985.
             Contributions are expressed as $\Delta ion/\Delta alk$ where Δ is the difference
             between a pre-episode value and the concentration on a given day.
             Positive values denote contributions to an alkalinity depression
             whereas negative values represent alkalinity increases.

HARP LAKE

1000 METRES

PLASTIC LAKE

500 METRES

Algonquin Park

Whitney

Huntsville

Dorset

Bracebridge

Gravenhurst

▲ town centres

— highways

0   scale   60km

Dorset

1985 Harp 5

1984 Harp 0

1984 Harp 4
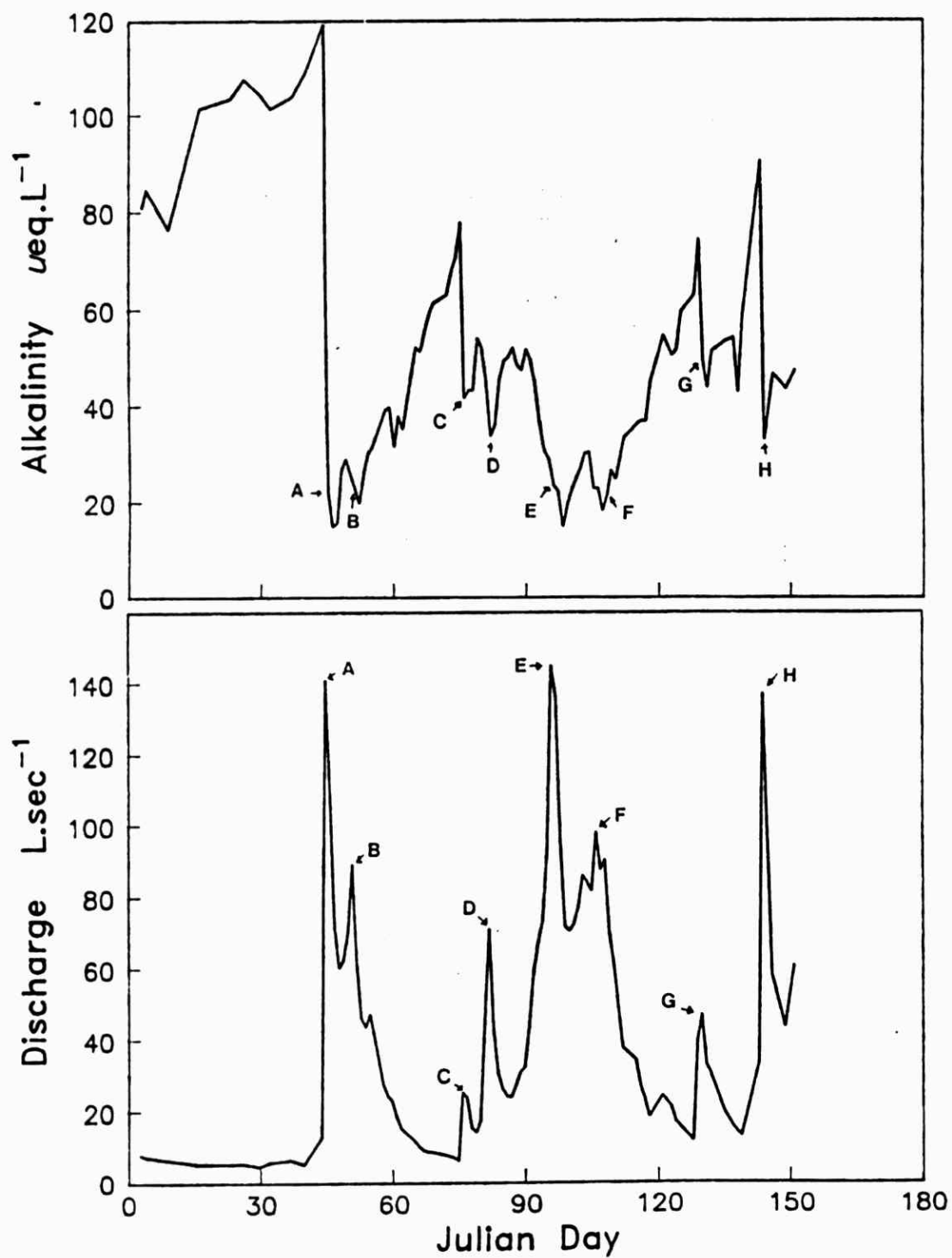
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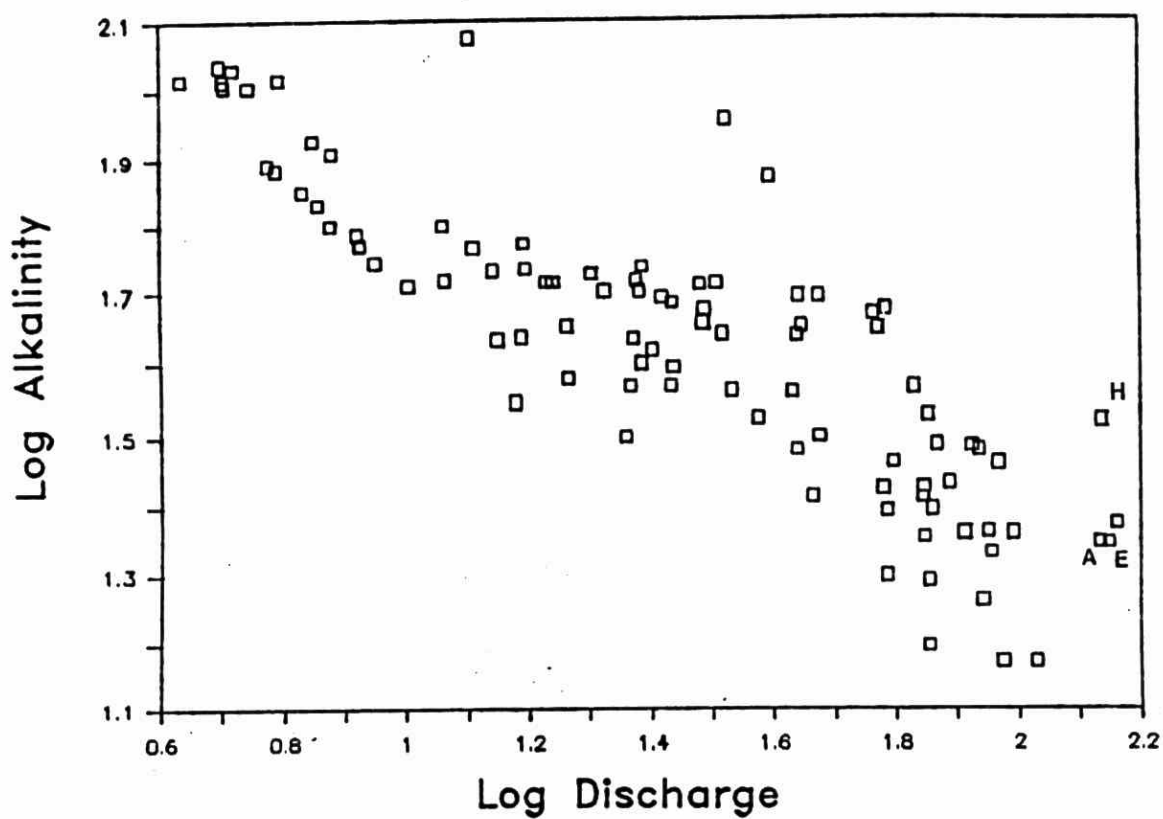
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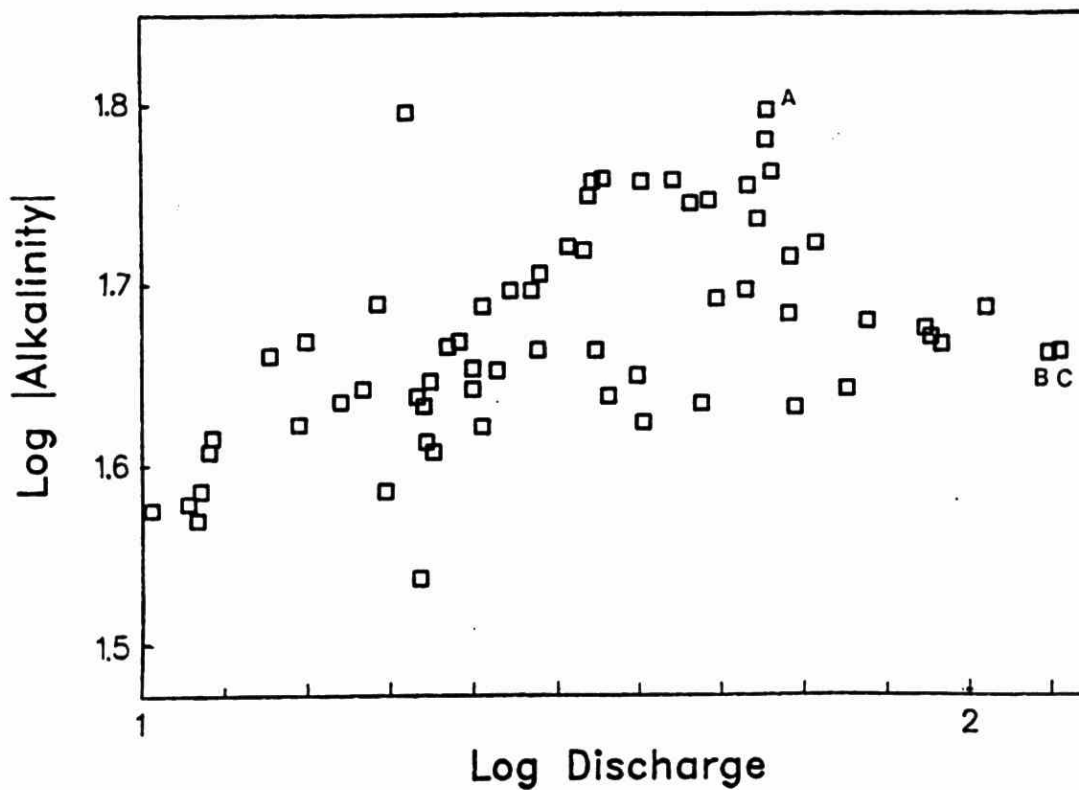
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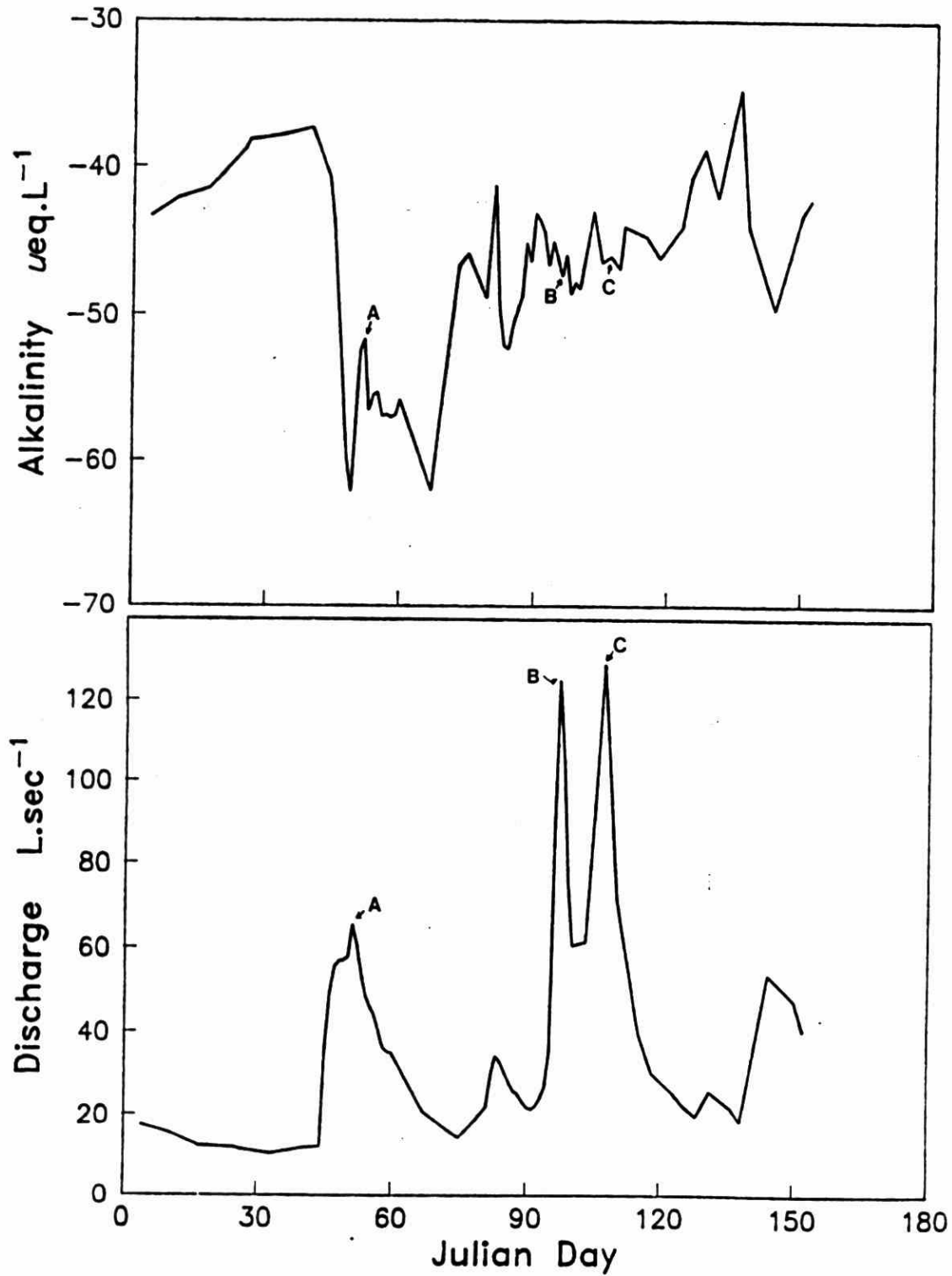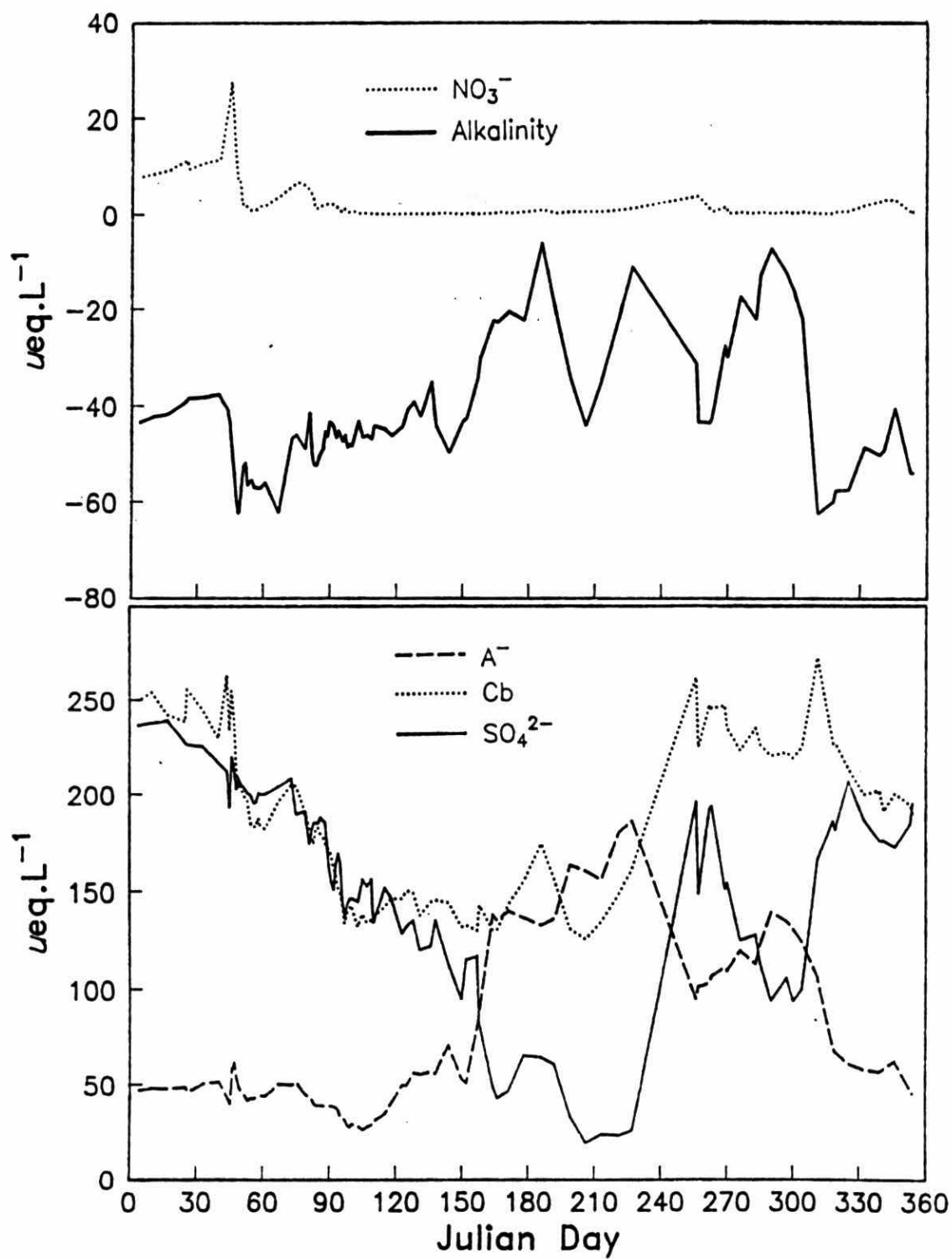
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1984 Harp O Episode #1
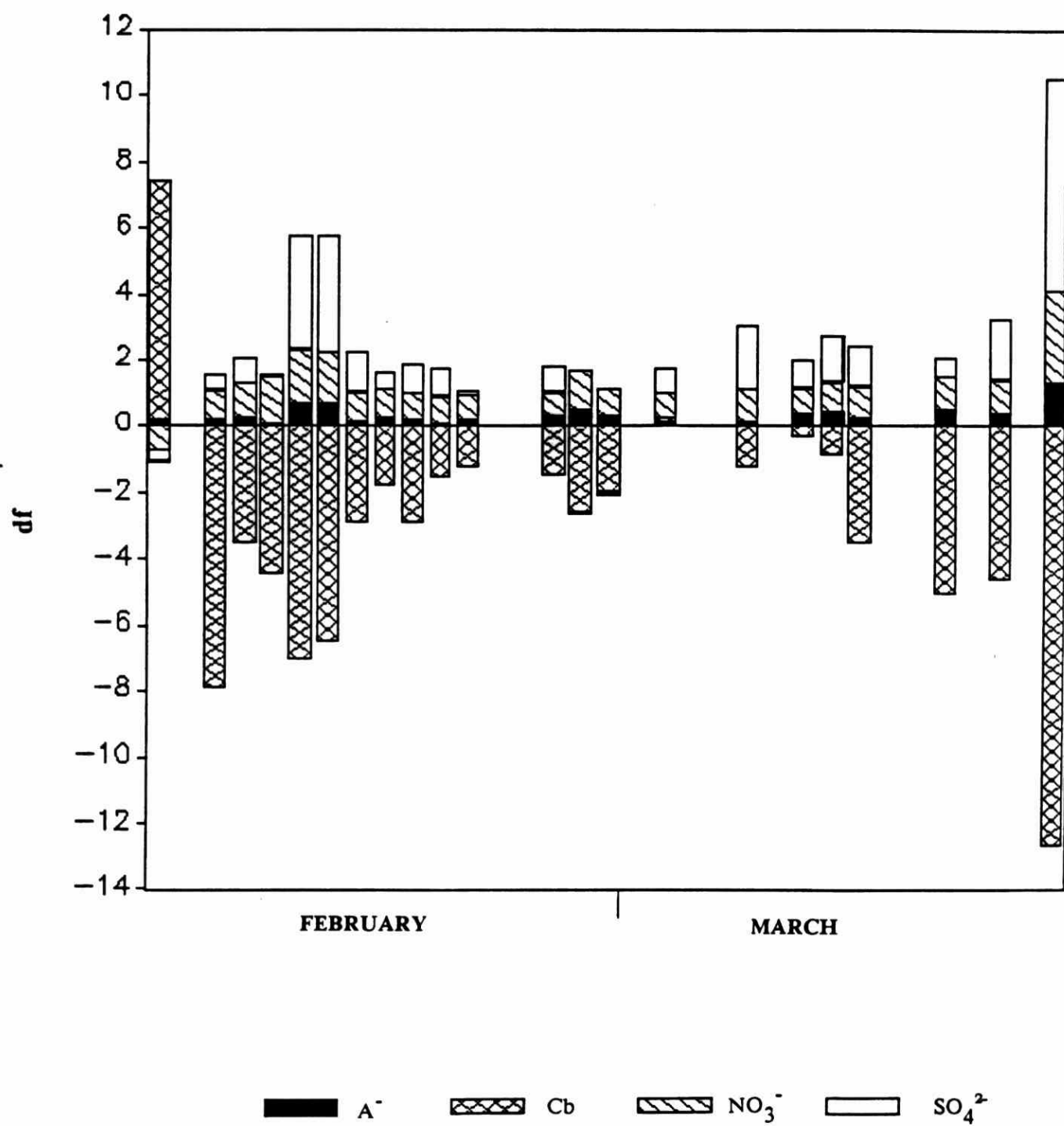
1984 Harp O Episode #2

1984 Harp 3

FEBRUARY   MARCH

A⁻   Cb   NO₃⁻   SO₄²⁻
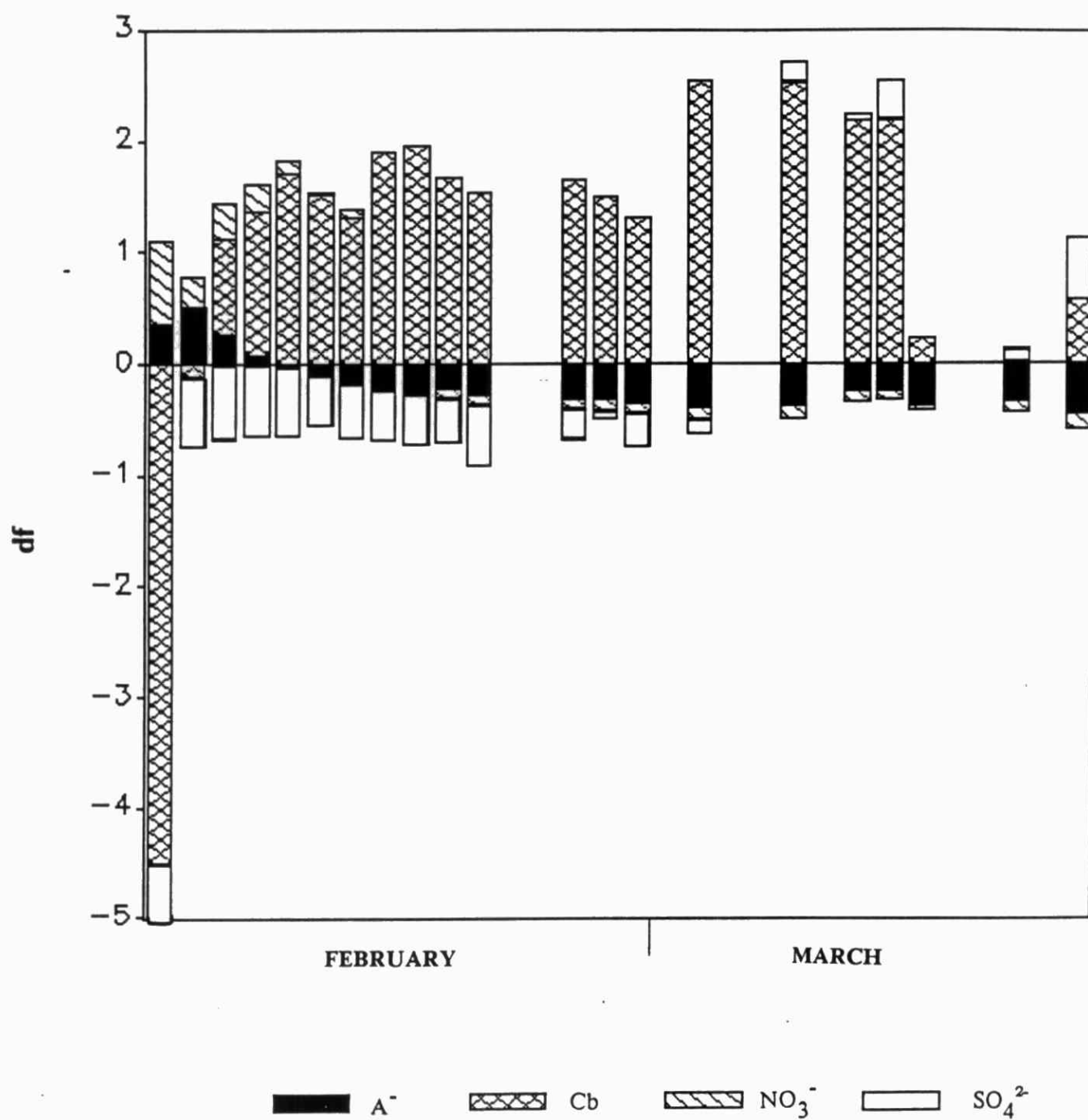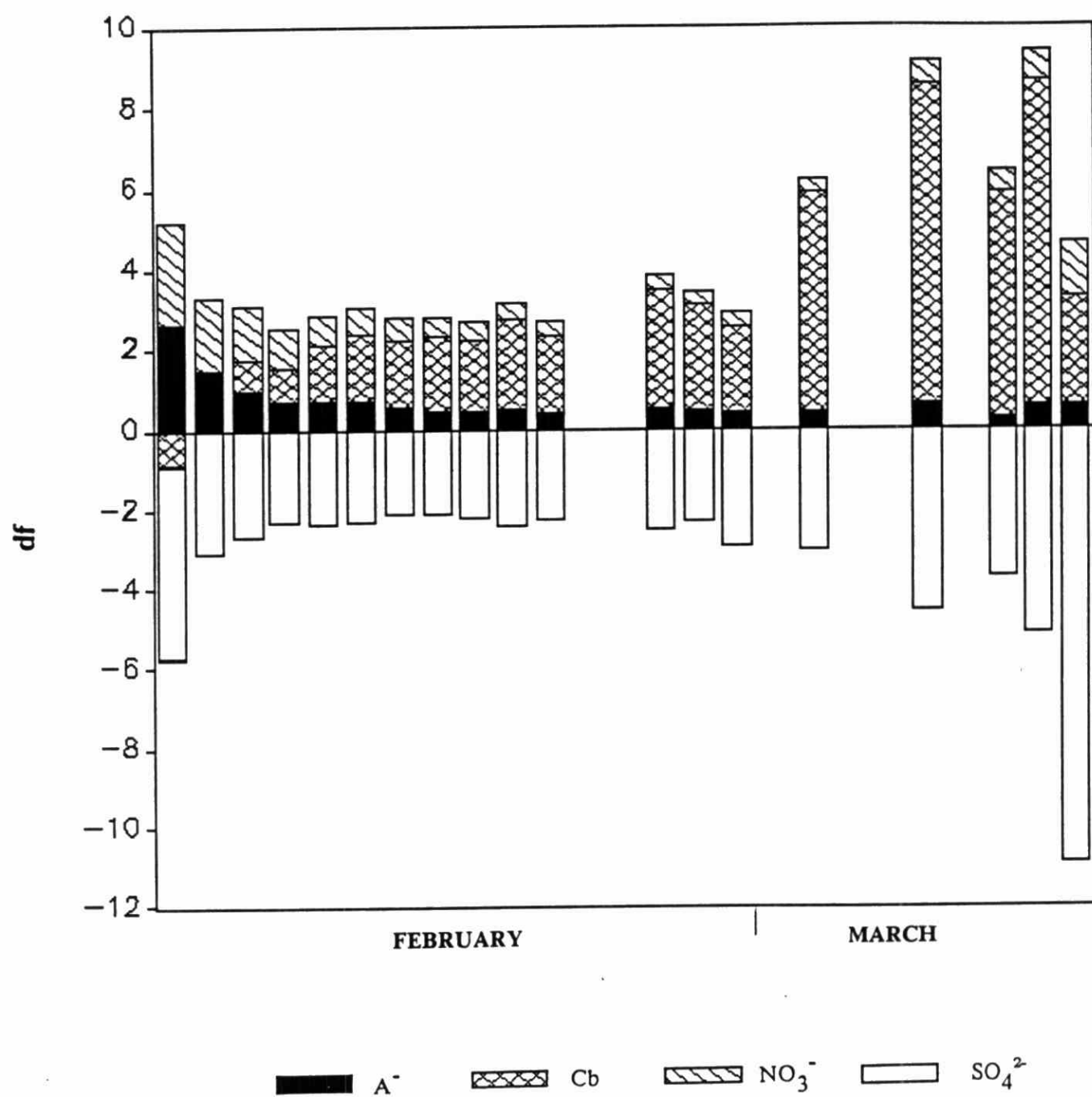
1984 Harp 3A

1984 Harp 4

1984 Harp 5

1984 Harp 6 Episode #1

1984 Harp 6 Episode #2

A⁻   Cb   NO₃⁻   SO₄²⁻

1985 Harp 0

df

MARCH   APRIL

■ A⁻   ▨ Cb   ▨ NO₃⁻   ▢ SO₄²⁻
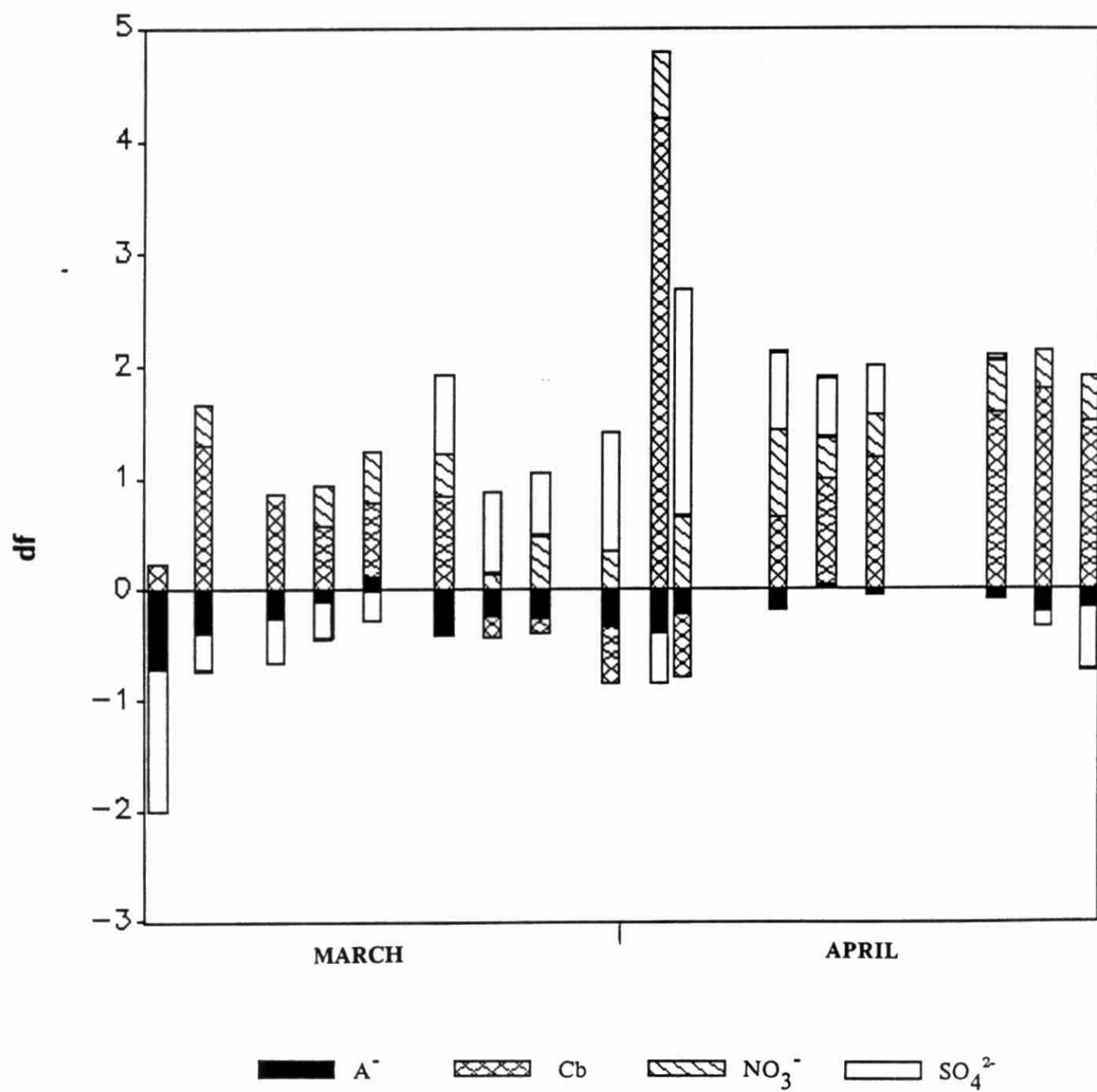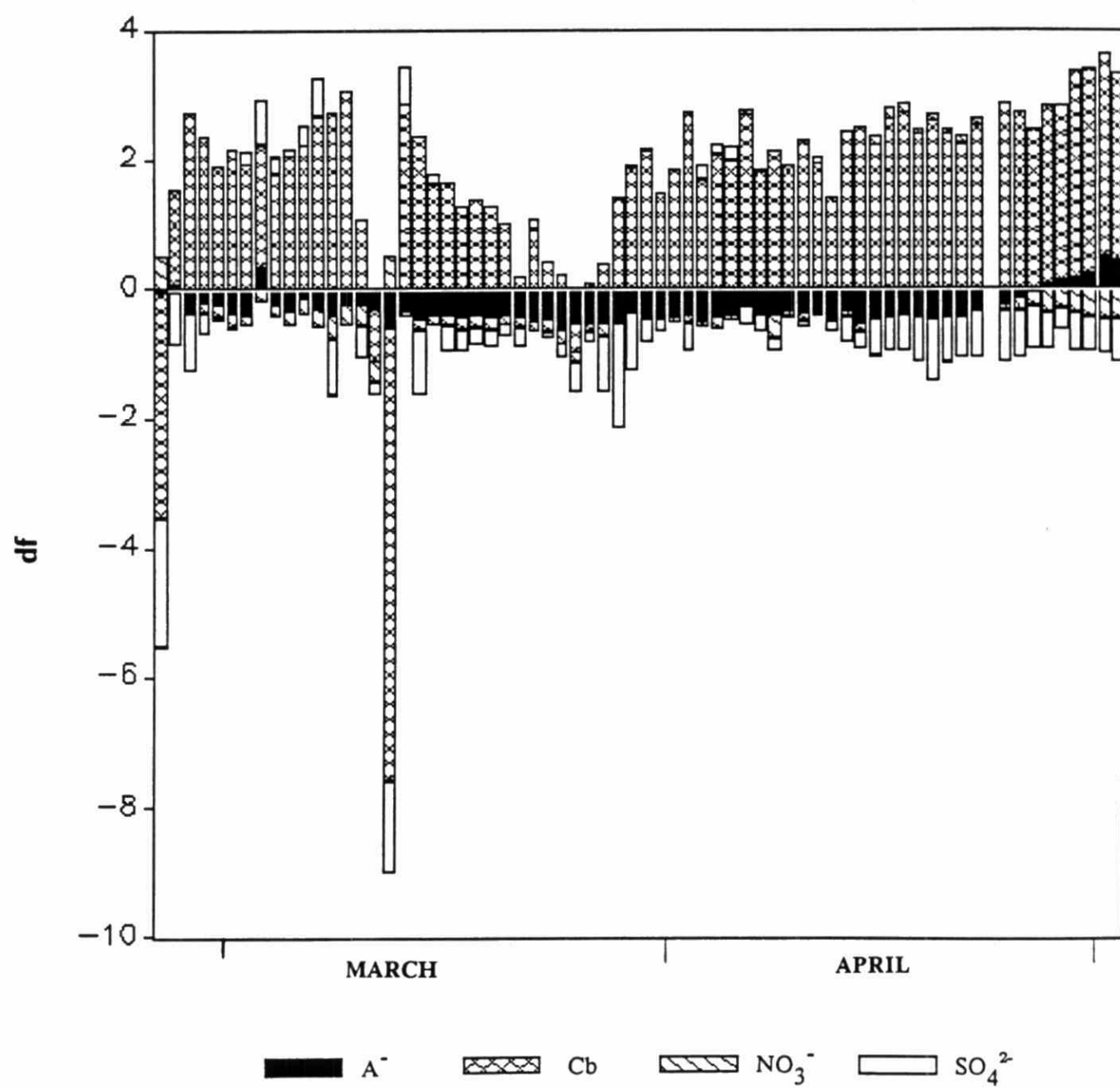
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1985 Harp 4

1985 Harp 6

1986 Harp 3
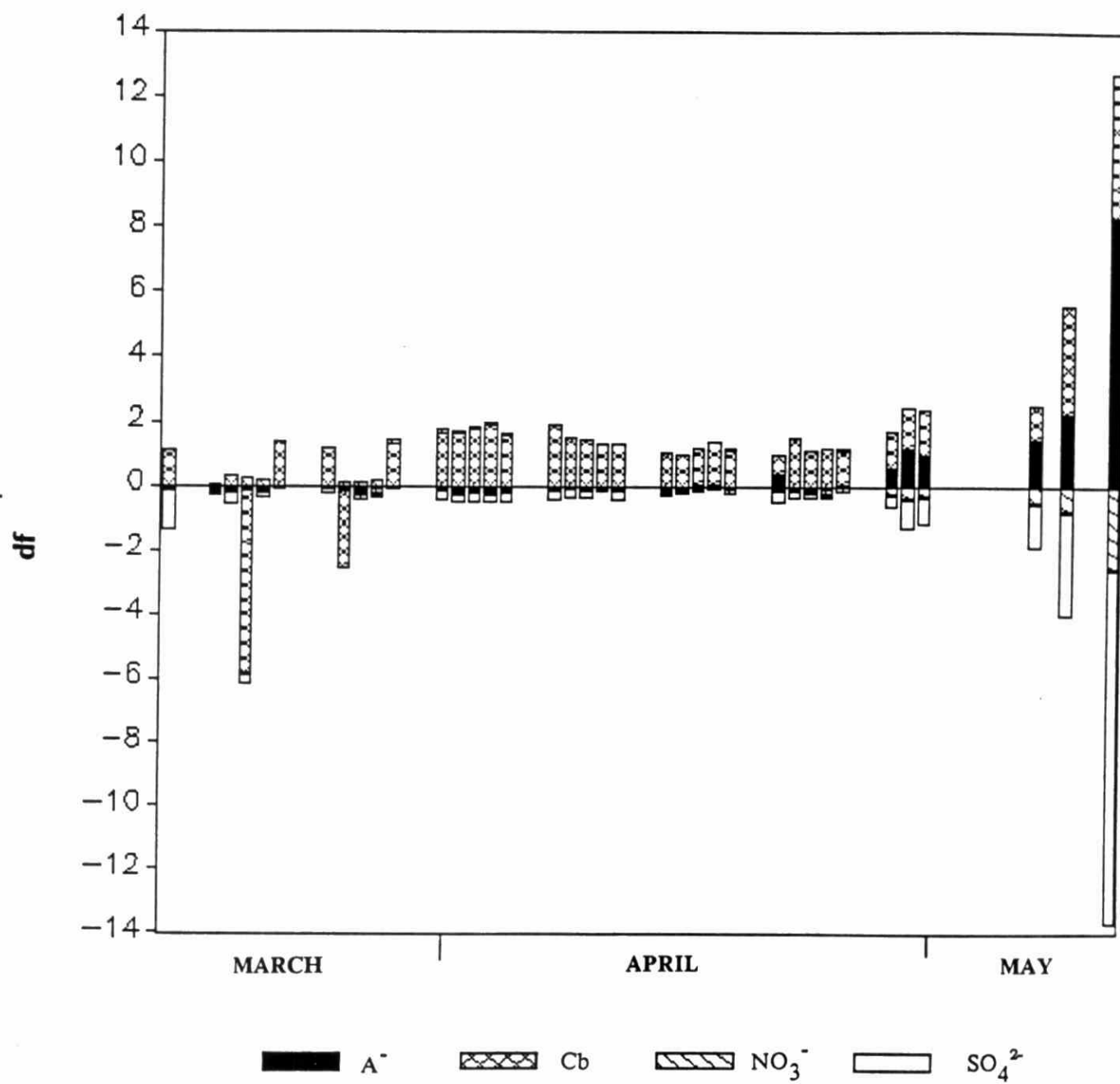
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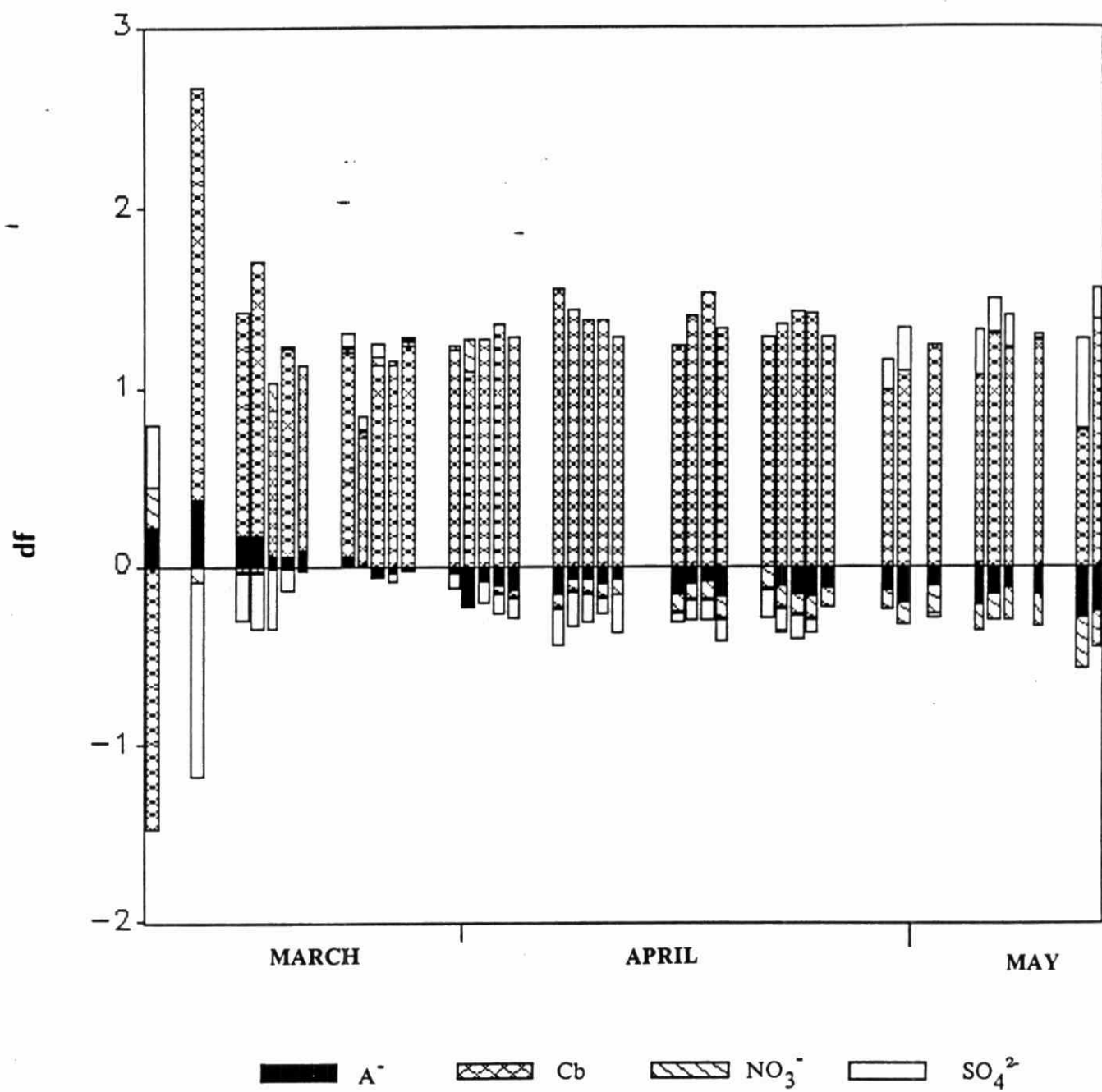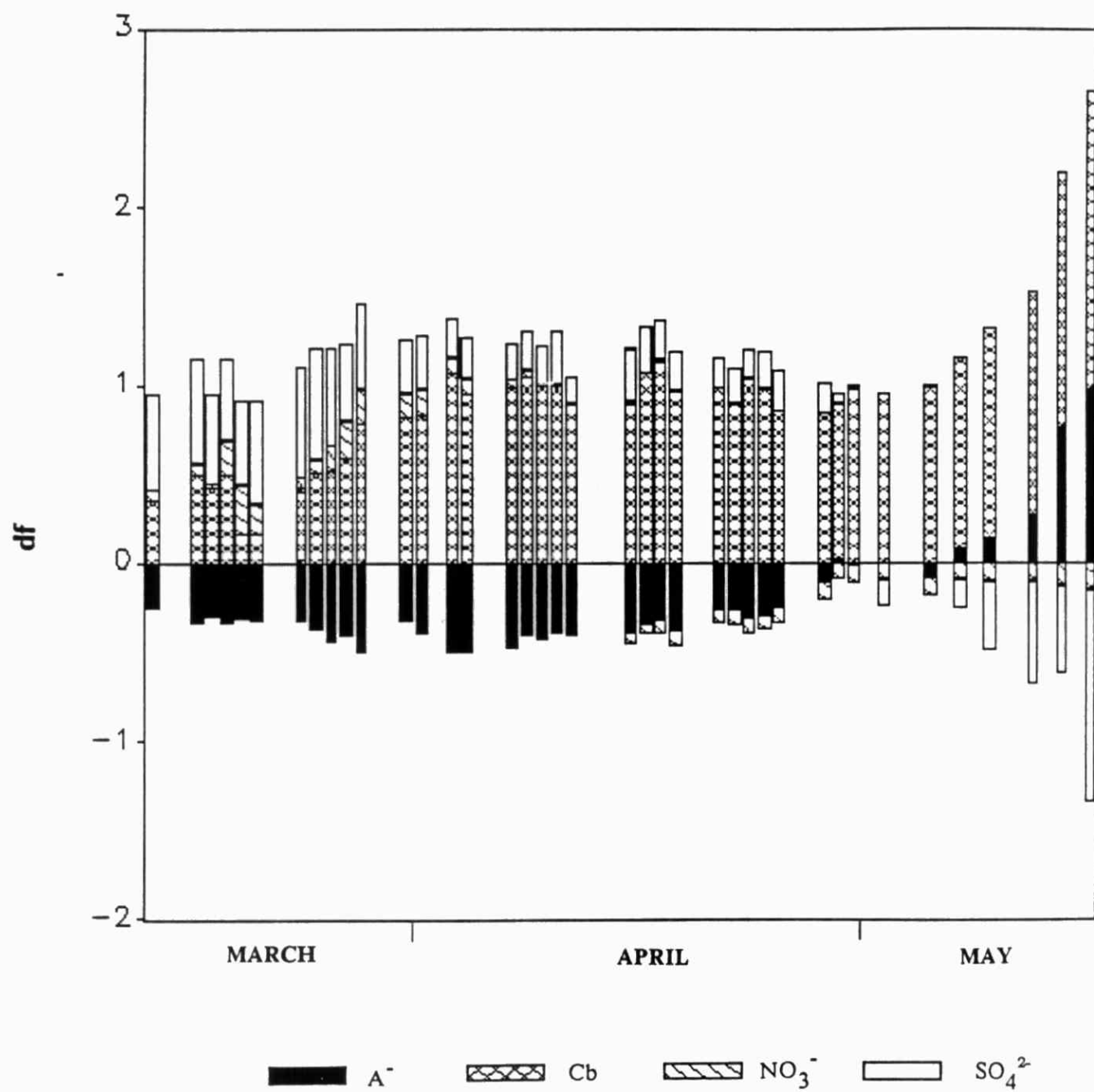
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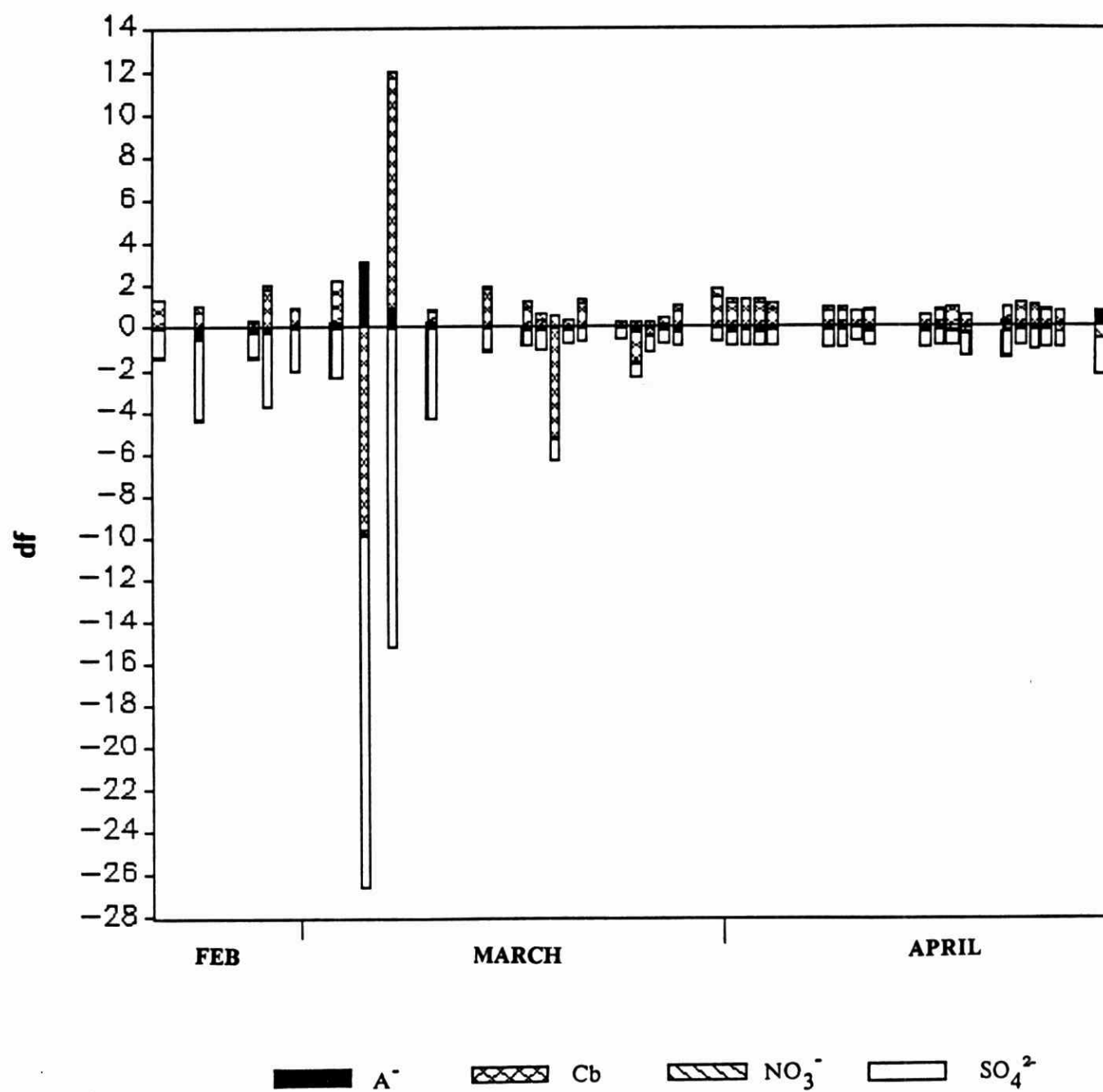
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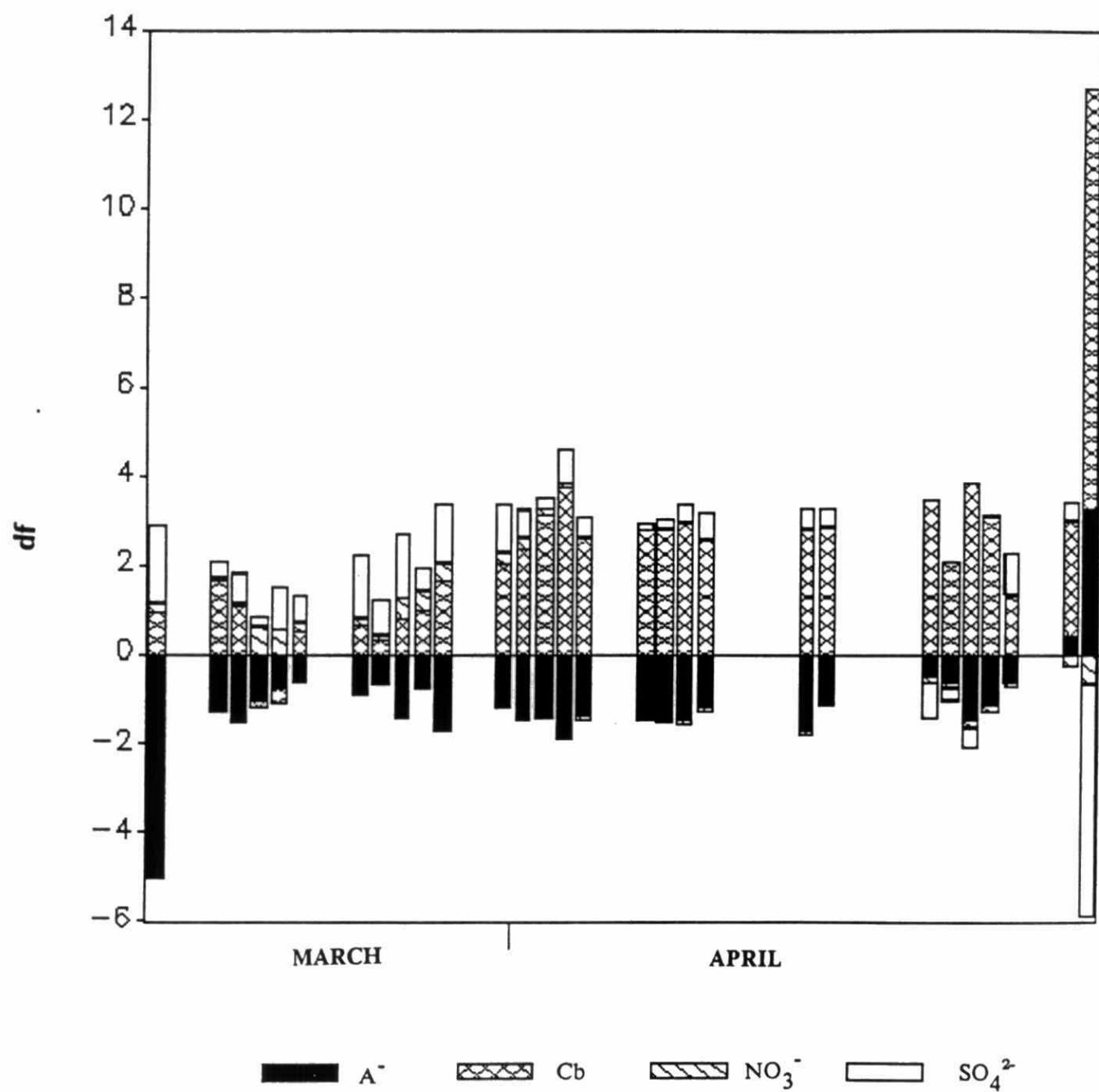
1984 Plastic 0

1984 Plastic 1

1985 Plastic   O

df

APRIL

A⁻   Cb   NO₃⁻   SO₄²⁻
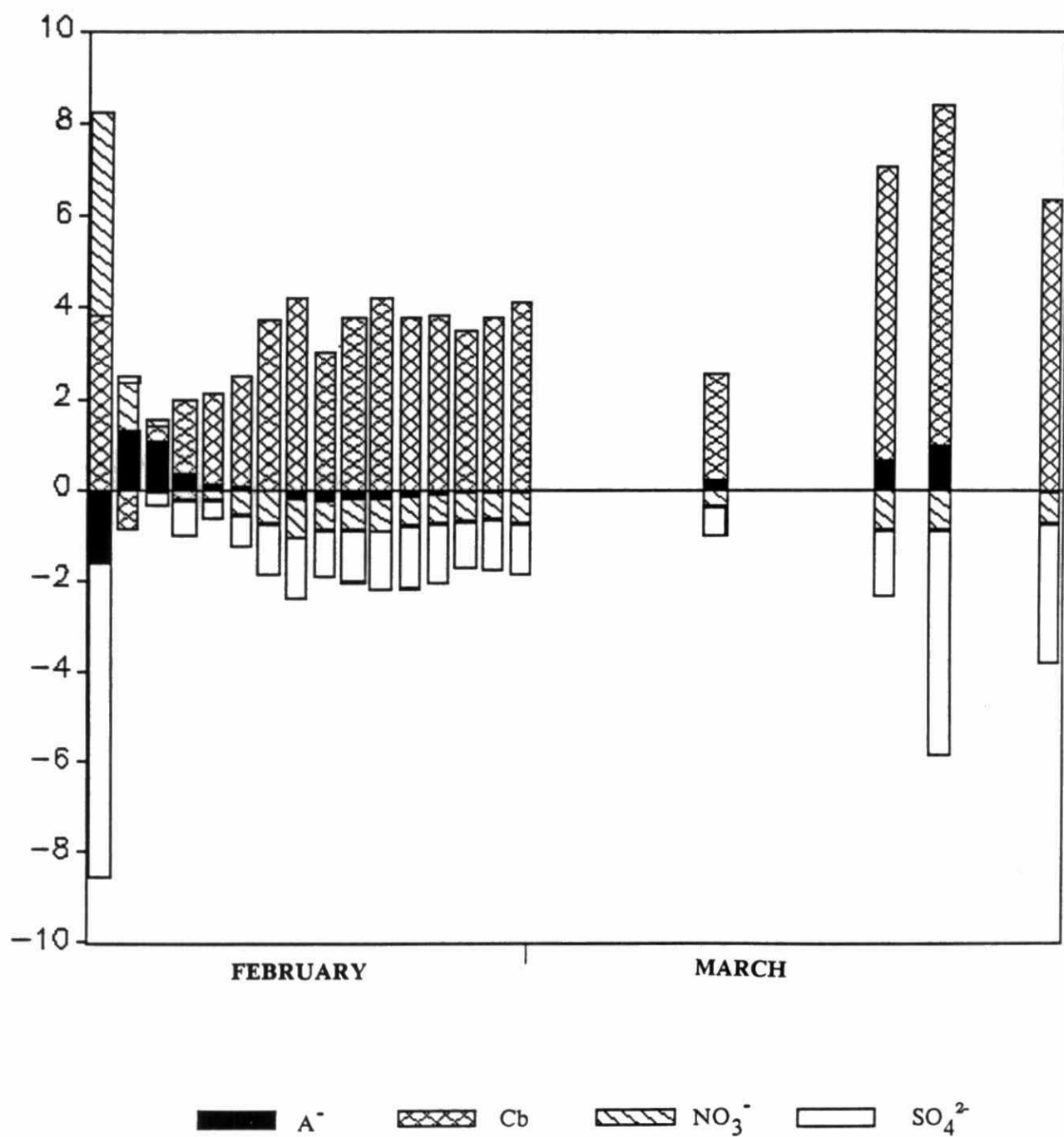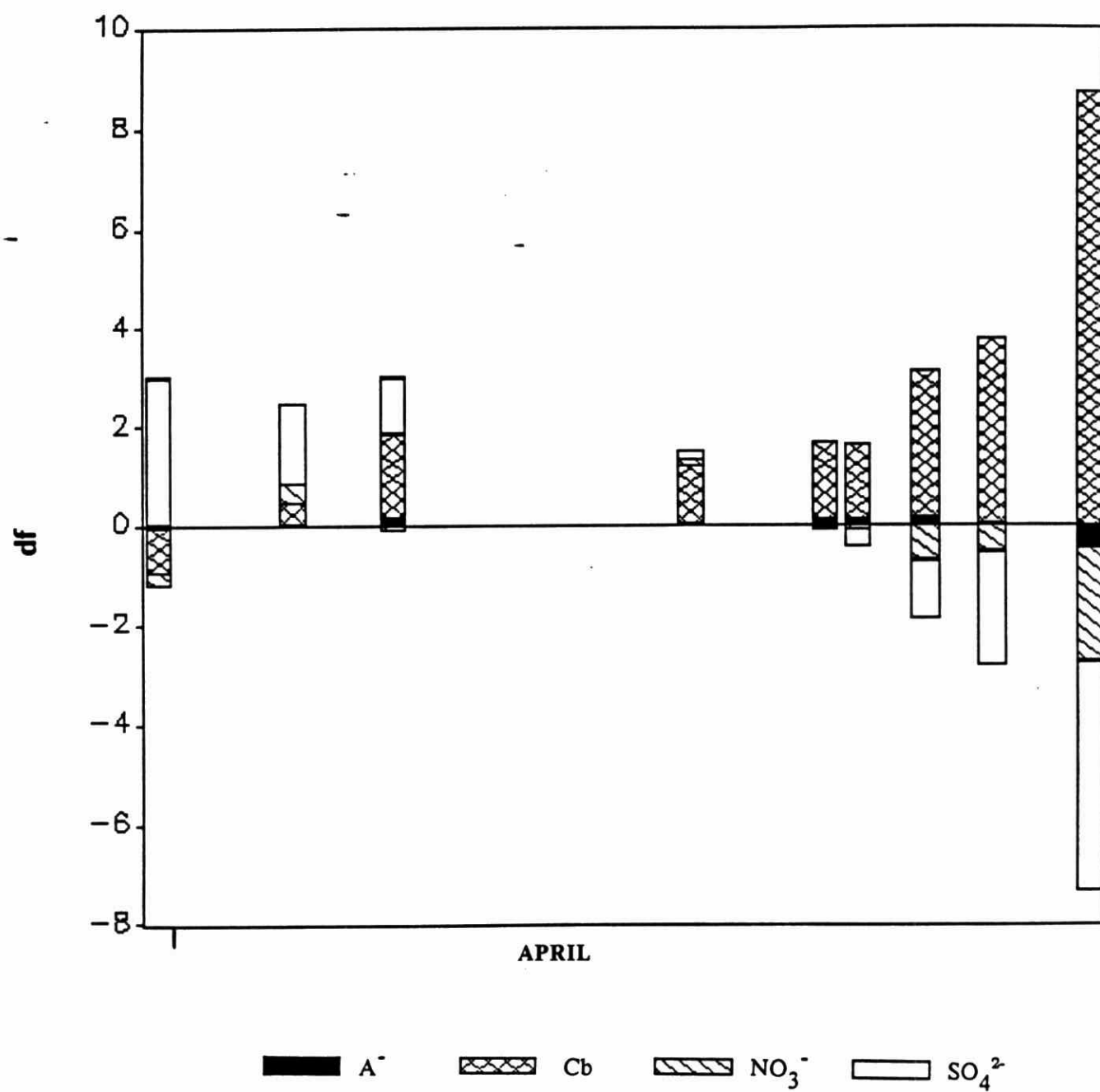
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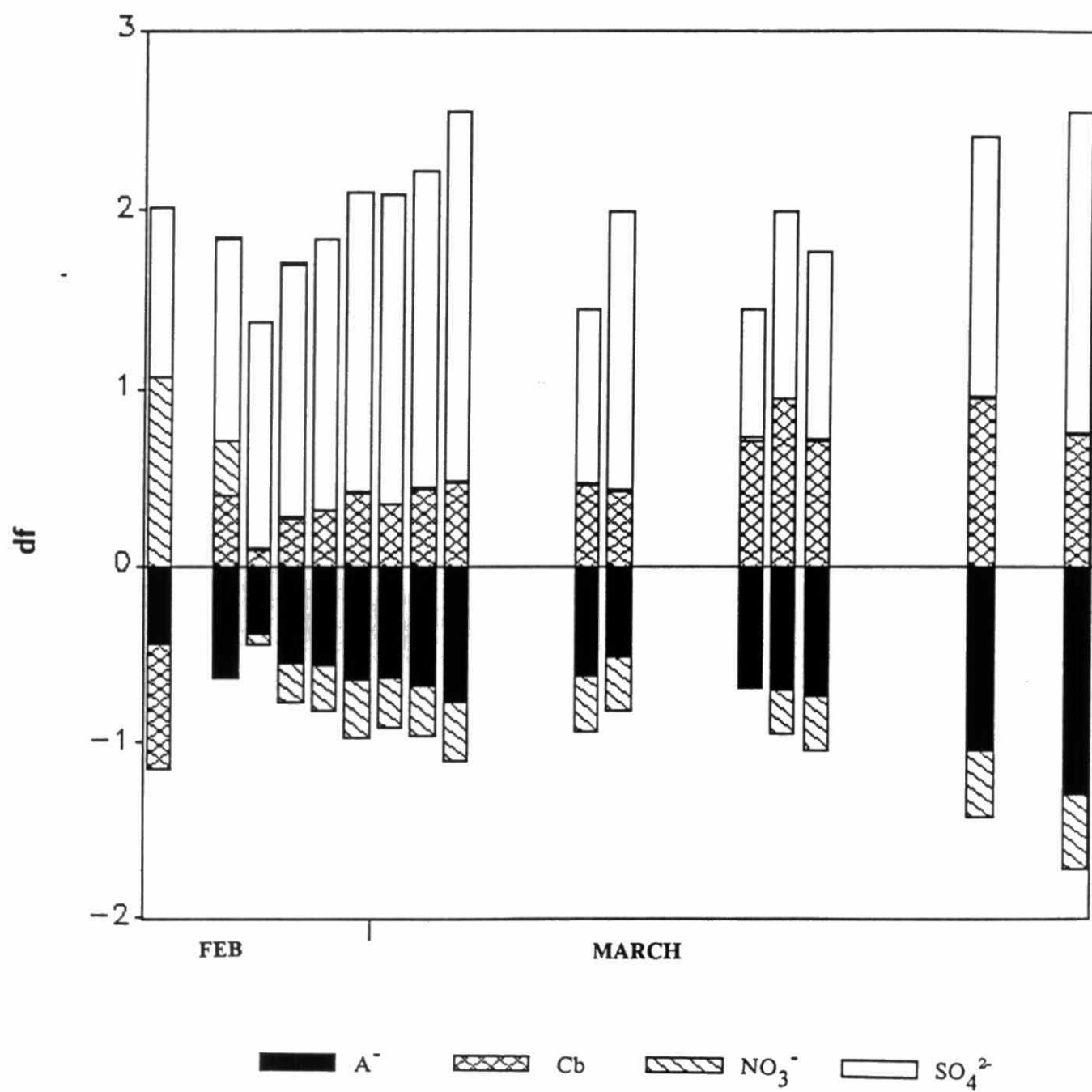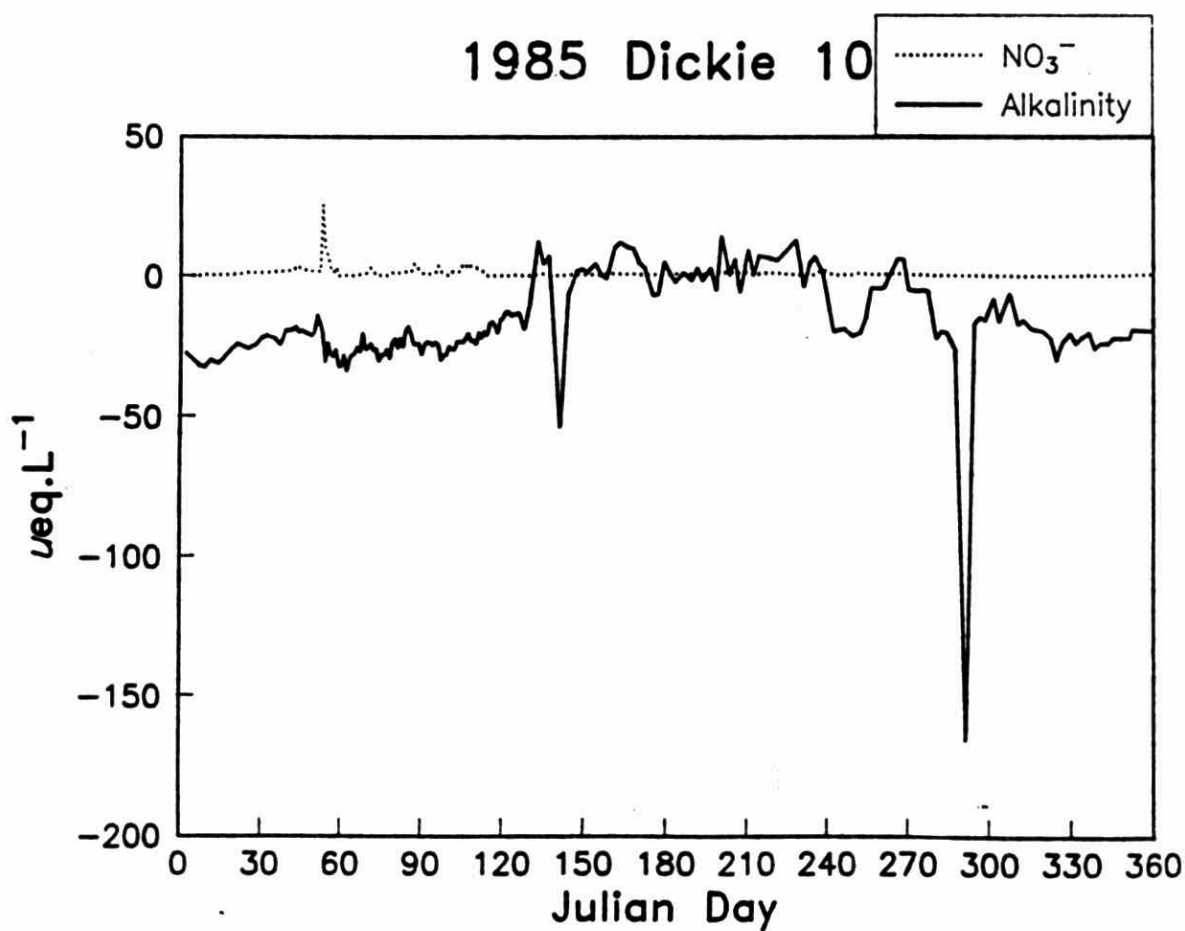
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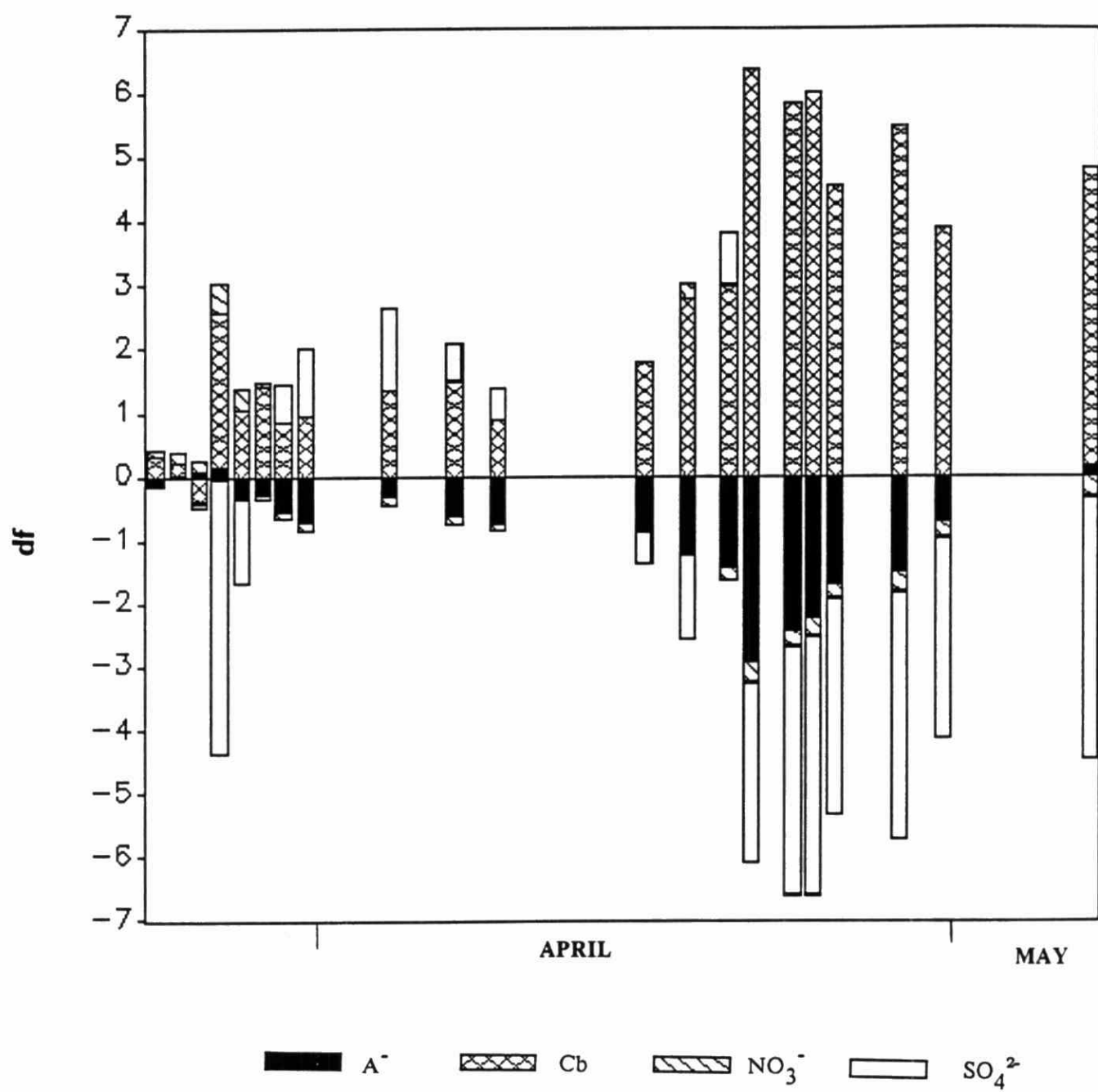
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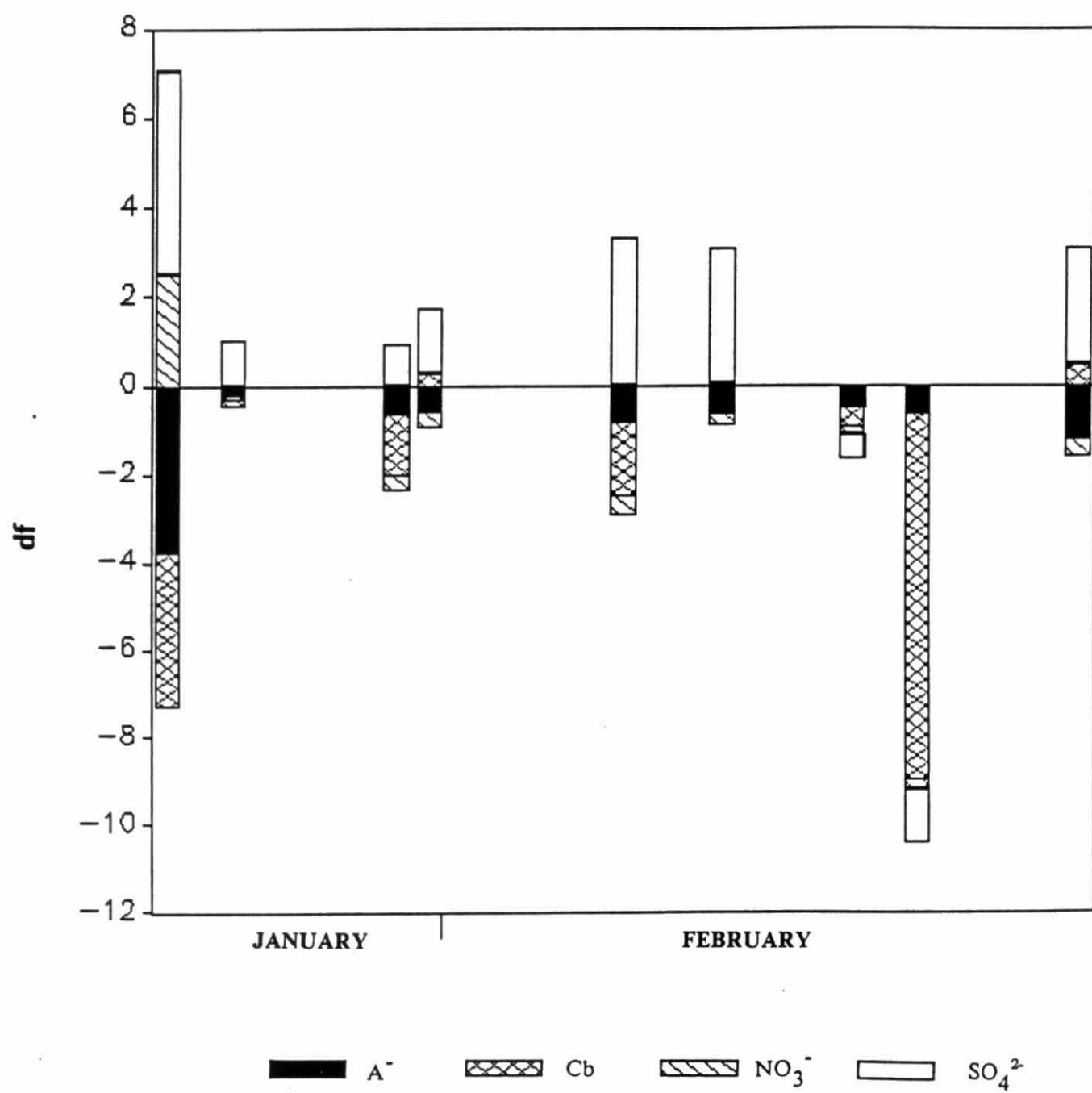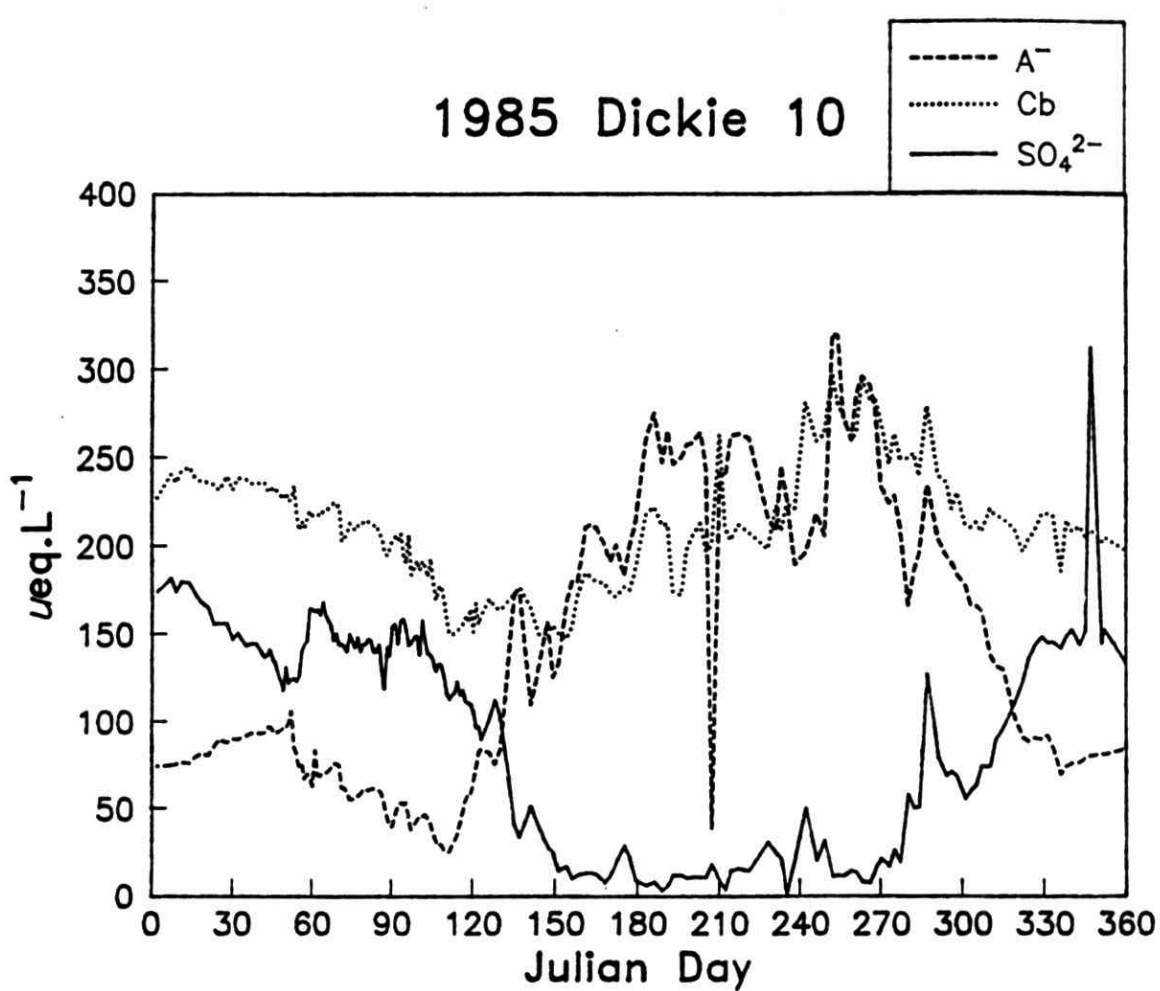
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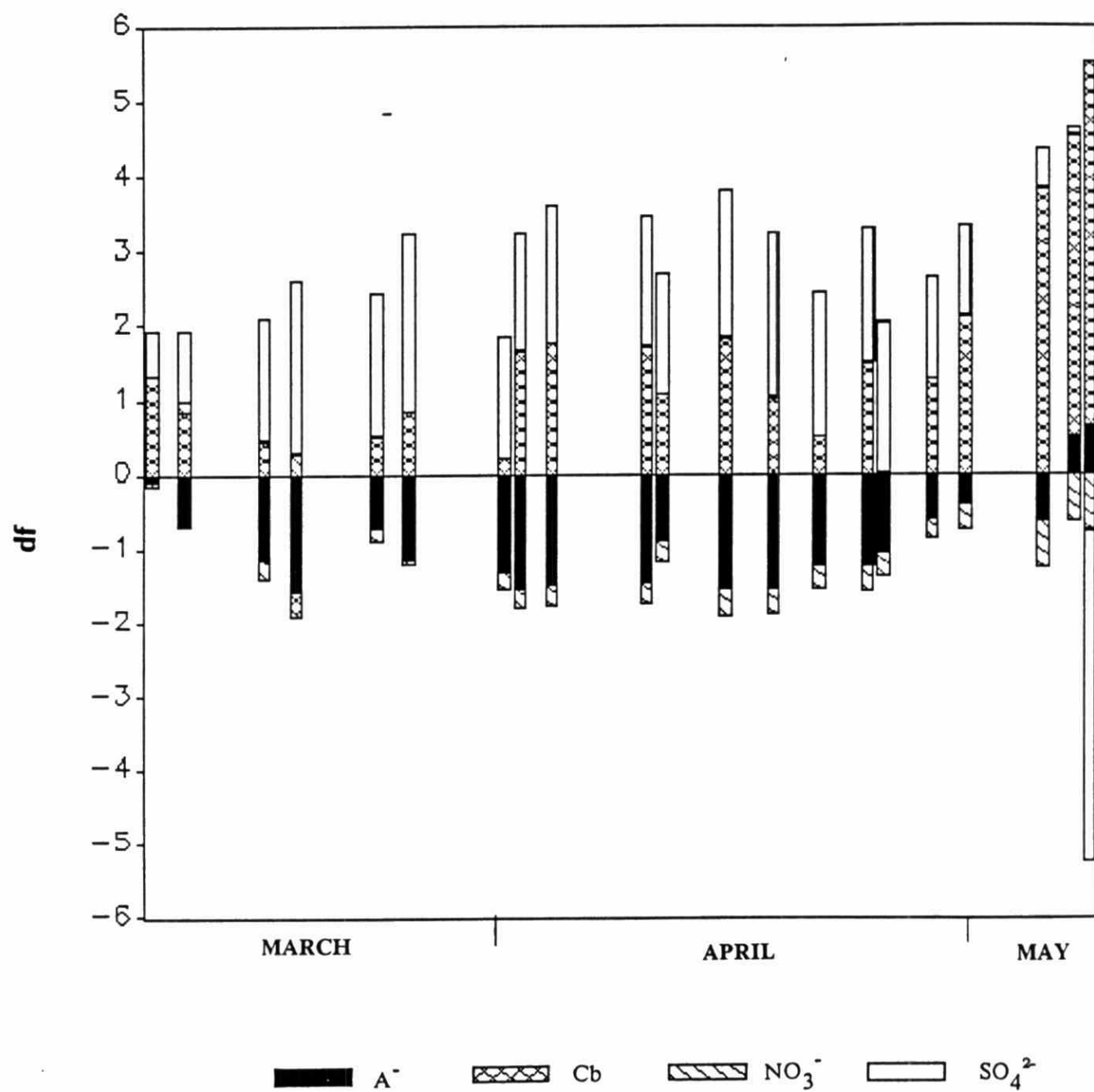
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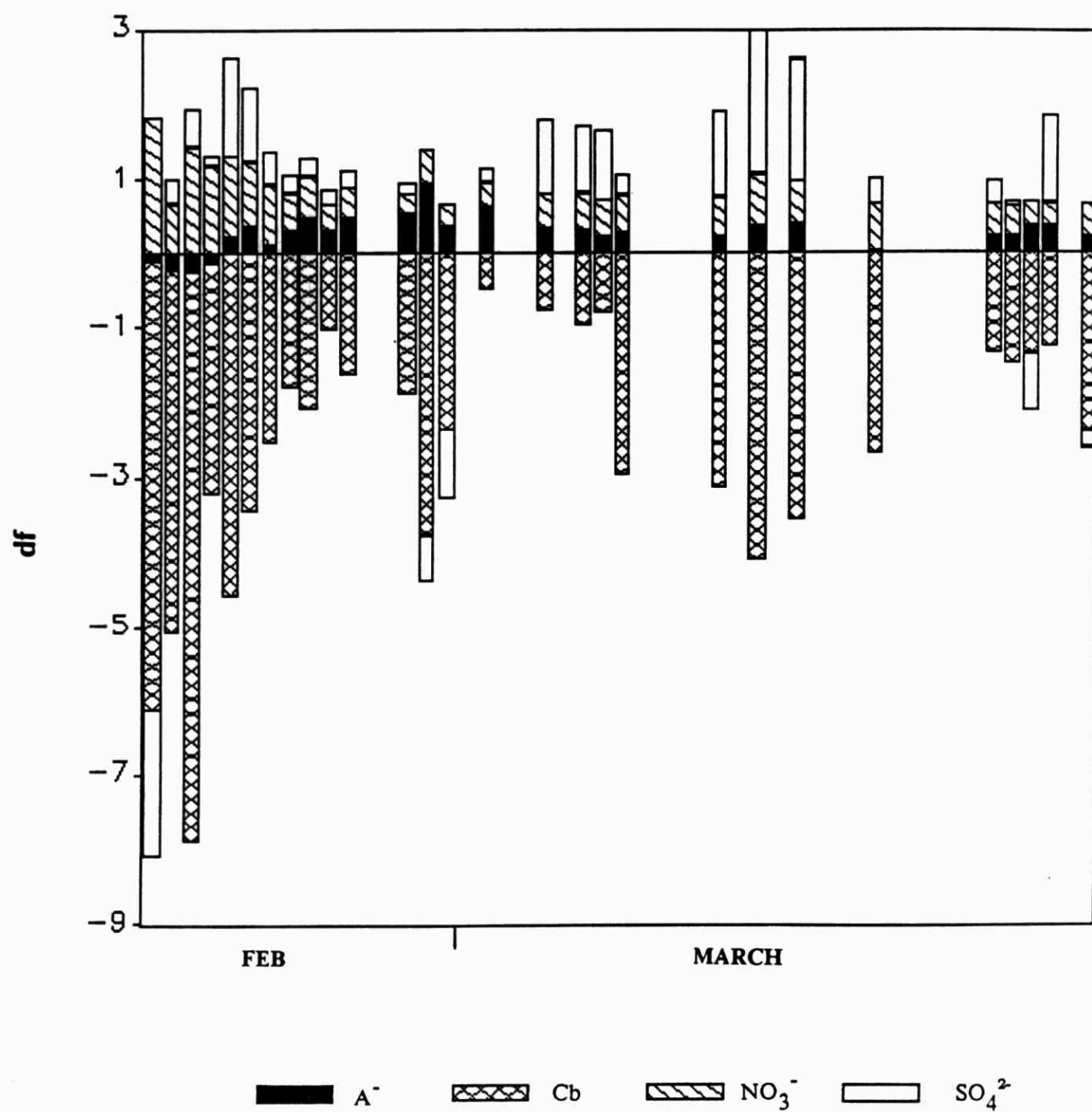
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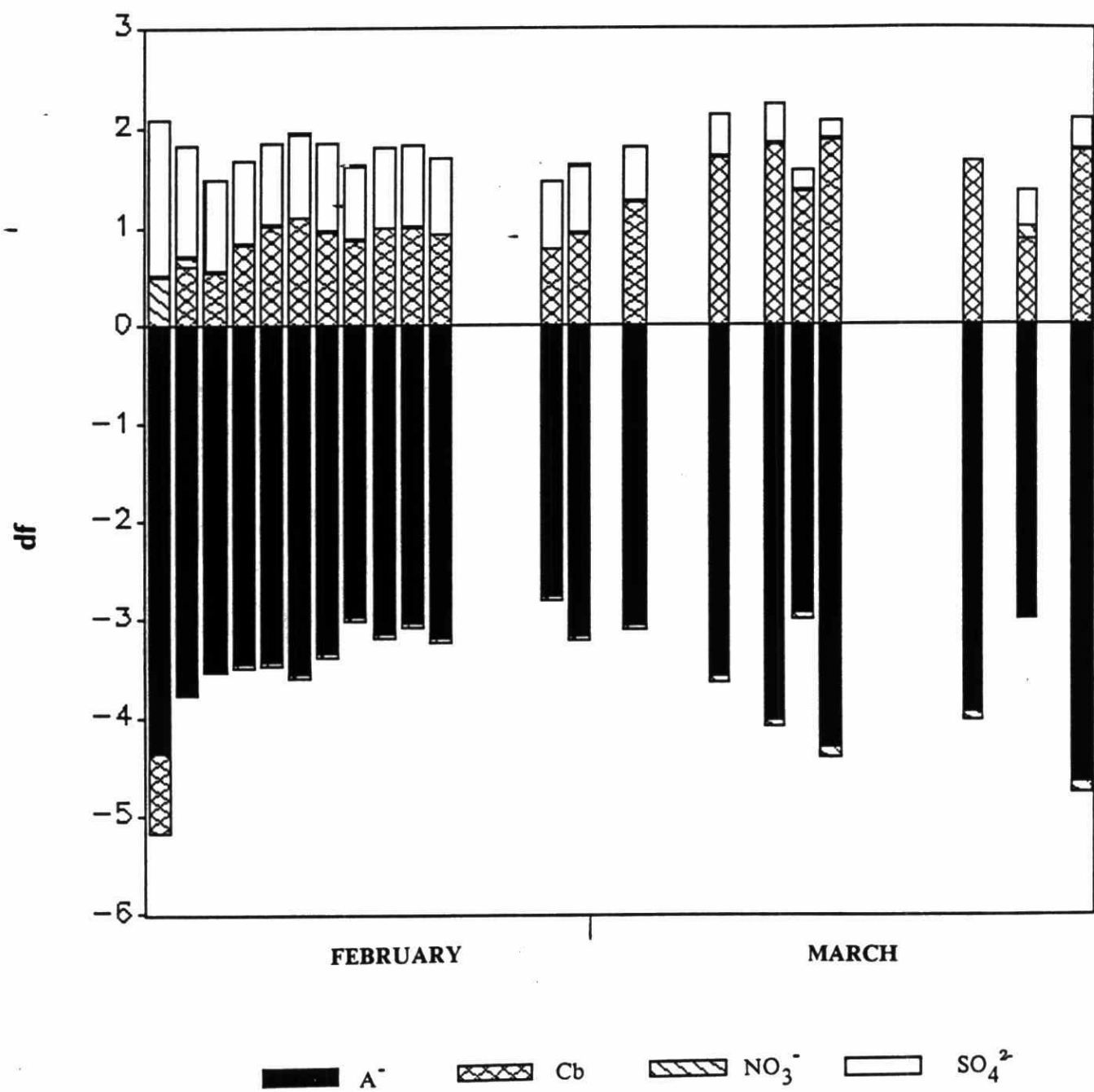
1984 Dickie 5 Episode #2

1984 Dickie 6

1984 Dickie 10

1984 Dickie 11

FEBRUARY   MARCH

A⁻   Cb   NO₃⁻   SO₄²⁻

1985 Dickie 0

1985 Dickie 6

df

FEBRUARY　　MARCH

A⁻　　Cb　　NO₃⁻　　SO₄²⁻

1986 Dickie 5

df

MARCH   APRIL

A⁻   Cb   NO₃⁻   SO₄²⁻
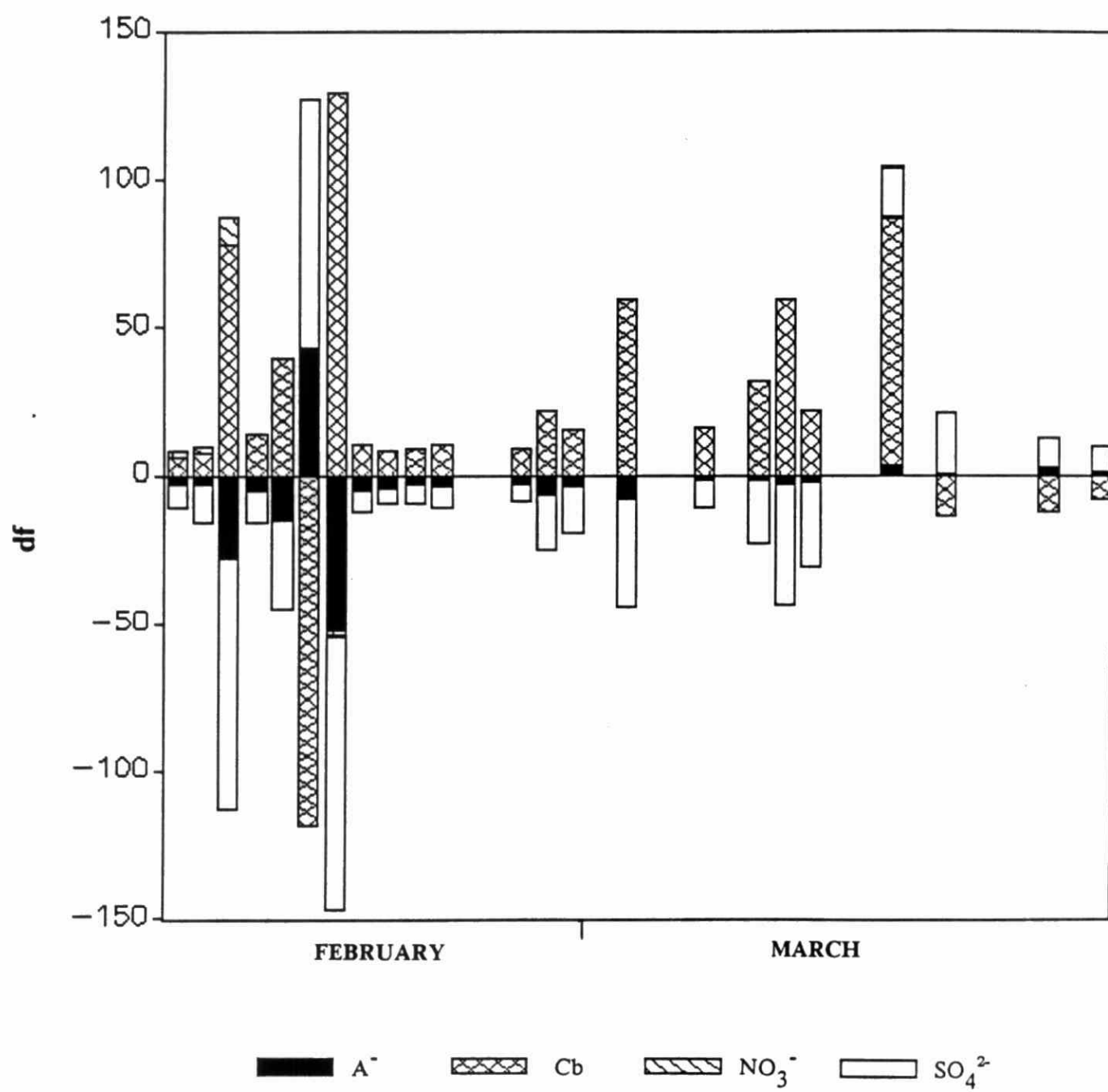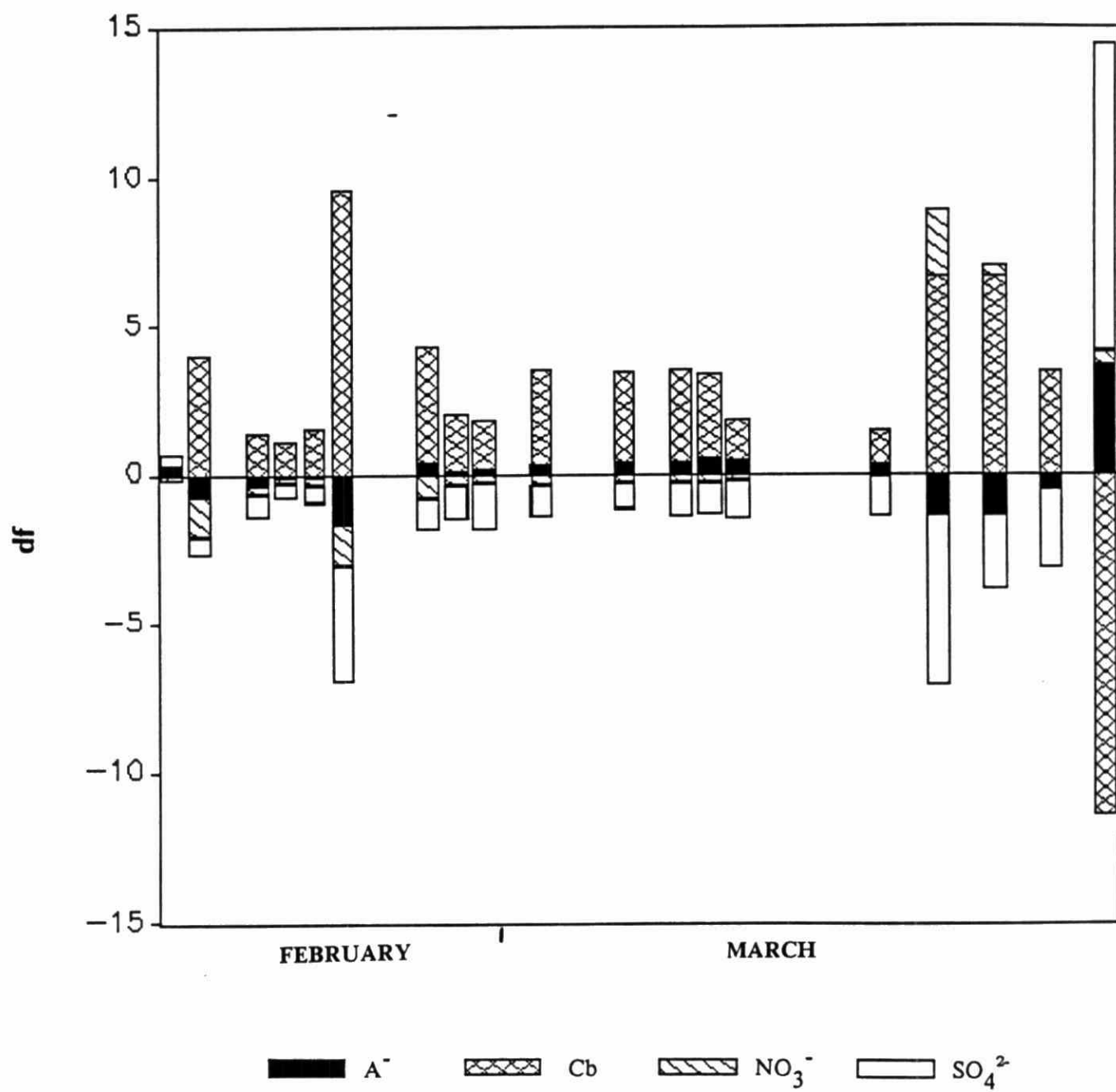
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1986 Dickie 6 Episode #2

df

MARCH

7   28
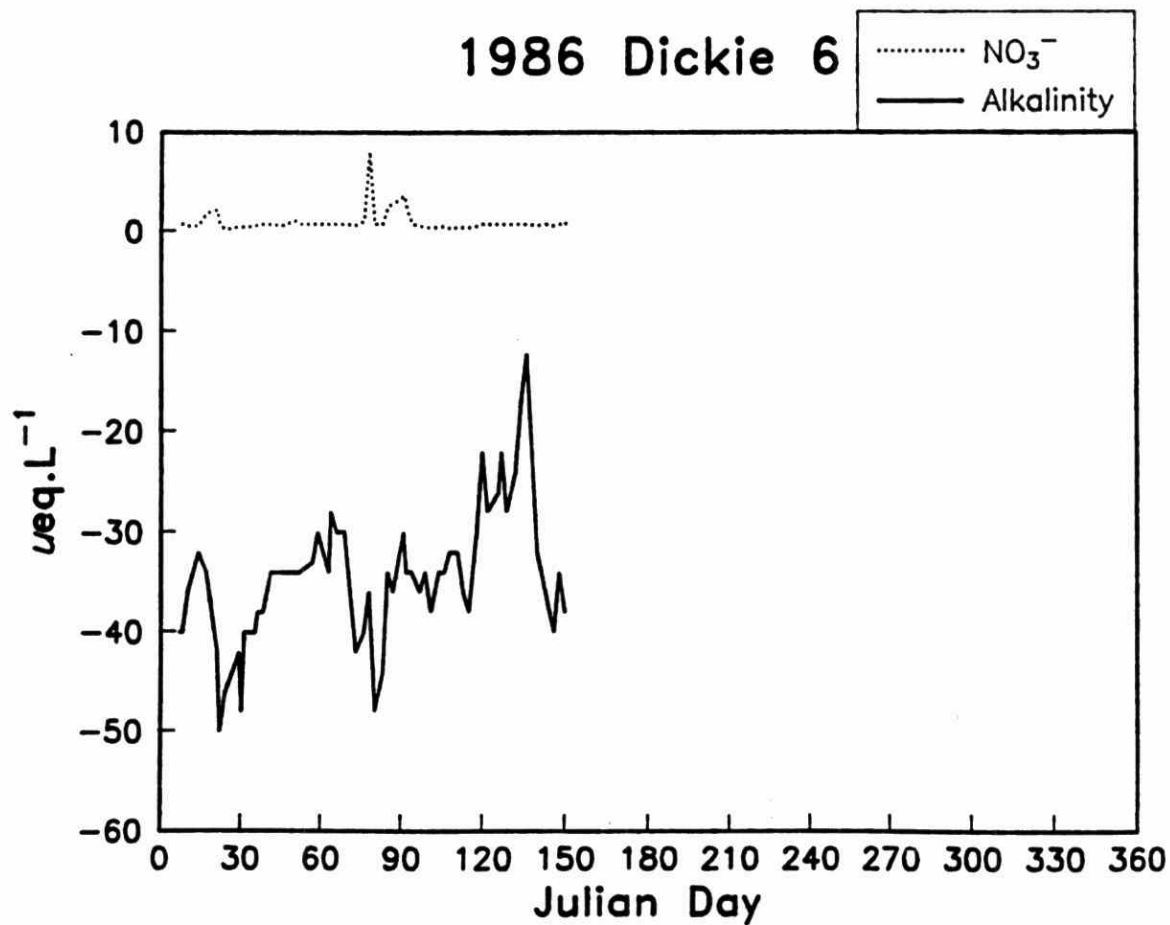
■■■ A⁻   ▨▨▨ Cb   ⟍⟍⟍ NO₃⁻   ☐ SO₄²⁻
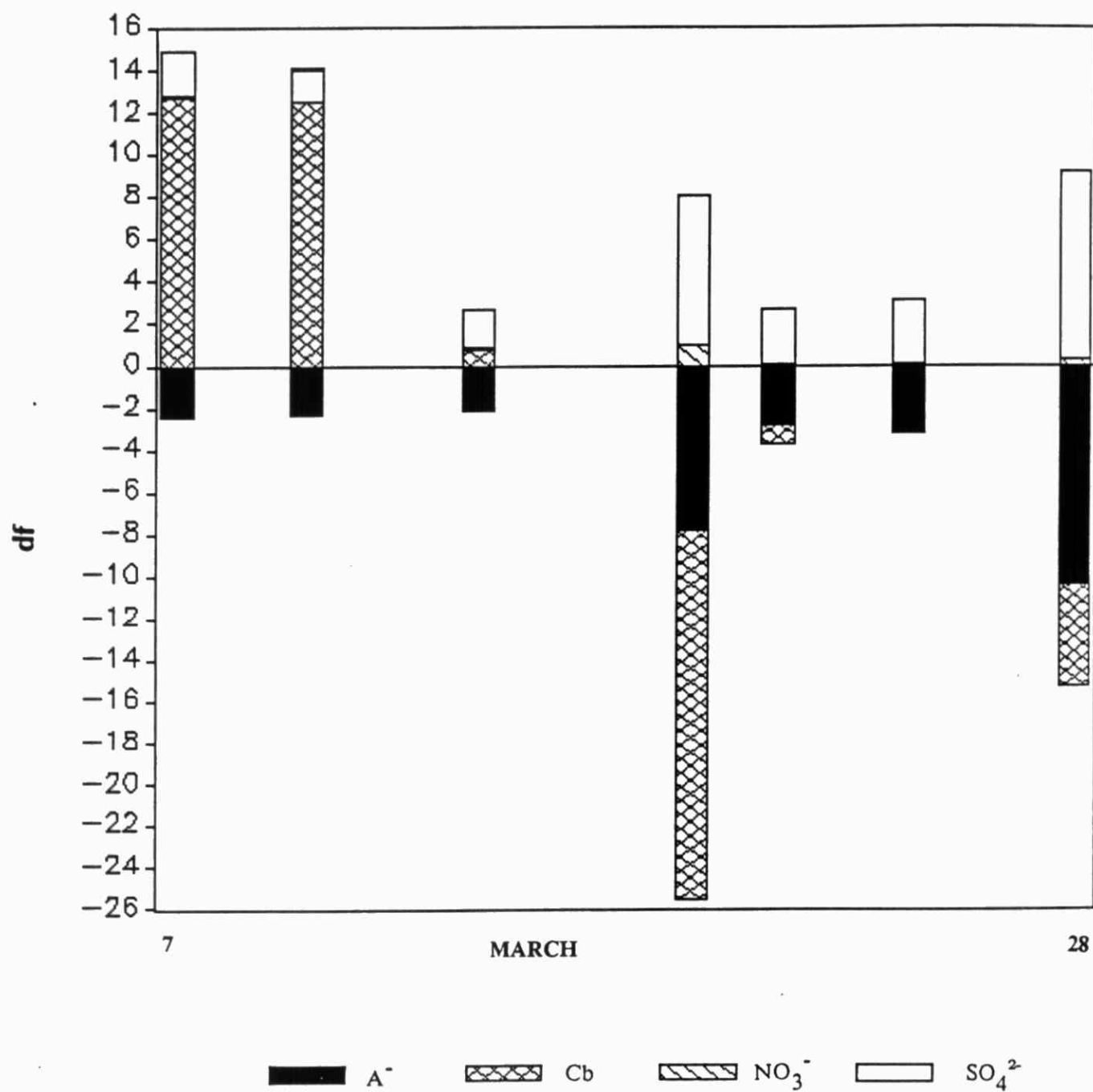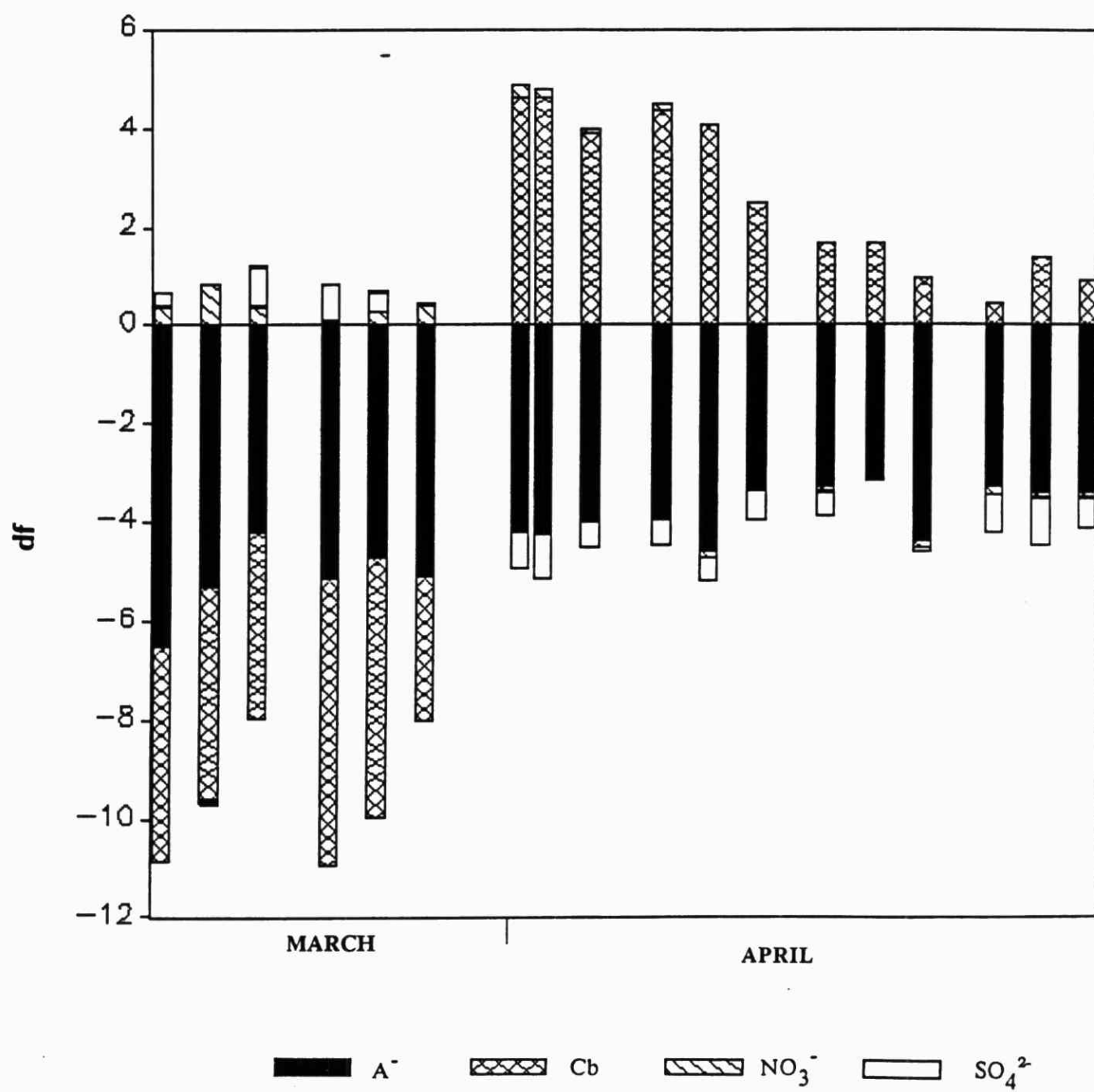
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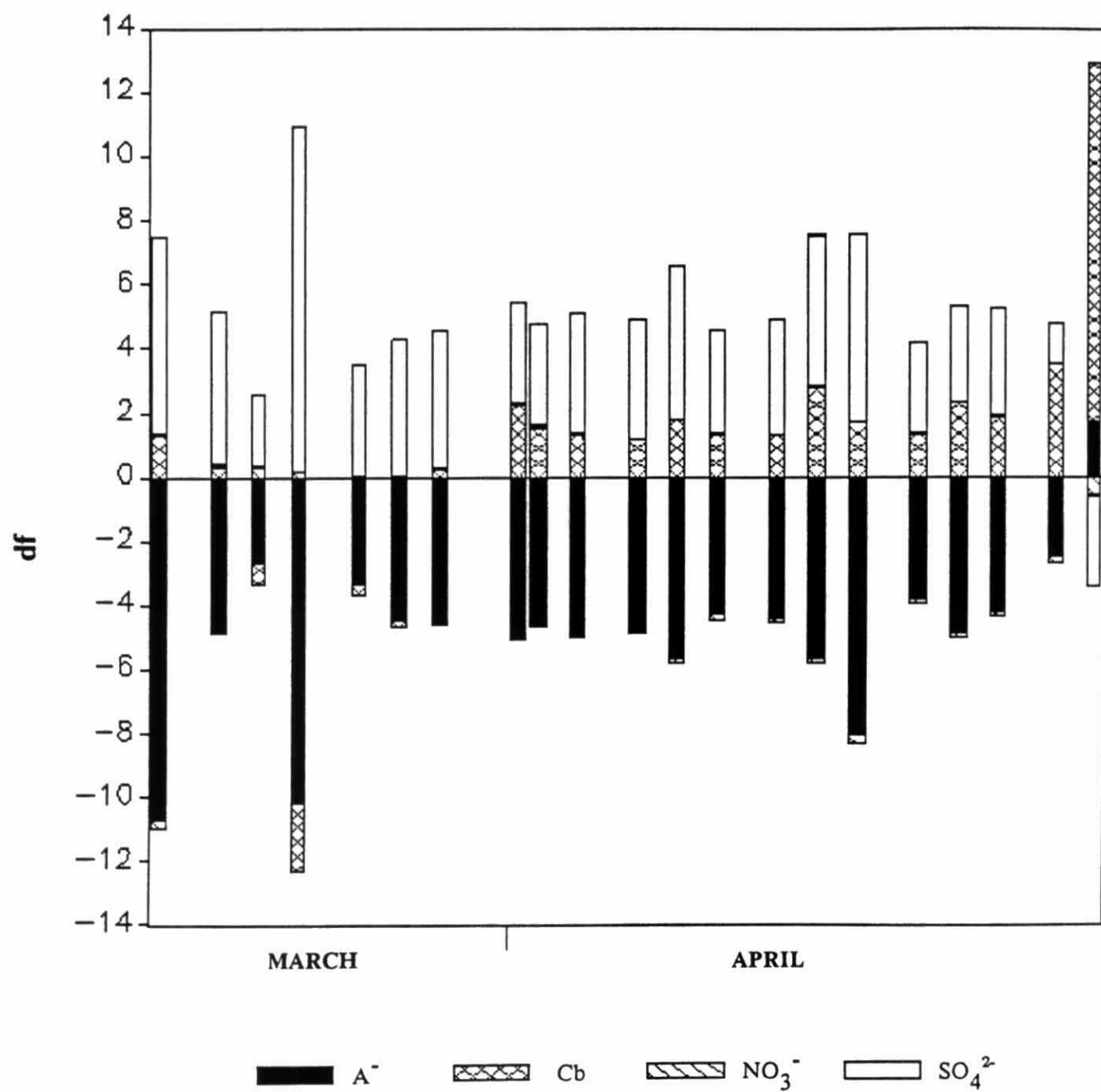
1984 Harp 3

1984 Harp 3

1984 Harp 3A

1984 Harp 3A

1984 Harp 4

1984 Harp 4

1984 Harp 5

1984 Harp 5

1984 Harp 6

1984 Harp 6

1984 Harp 6A

1984 Harp 6A

1985 Harp 0

1985 Harp 0

1985 Harp 3

1985 Harp 3

1985 Harp 4

1985 Harp 4

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1985 Harp 6

1985 Harp 6A

1985 Harp 6A
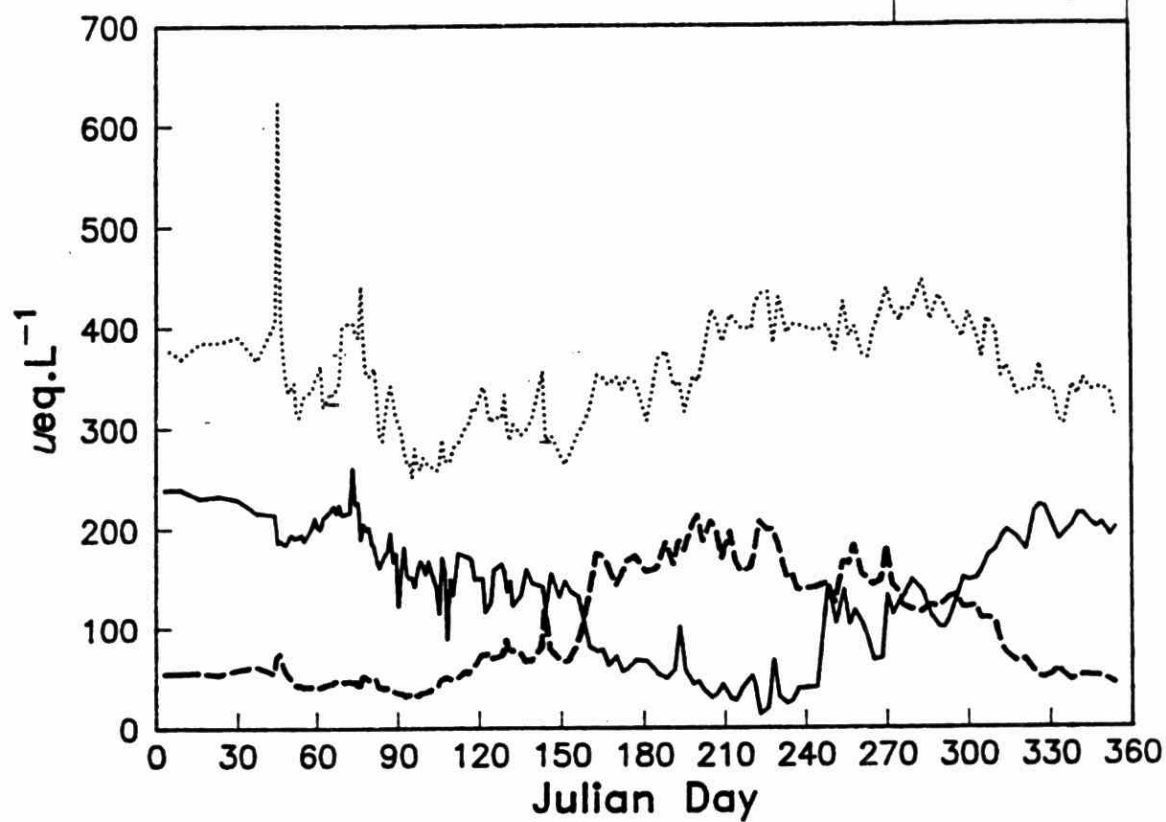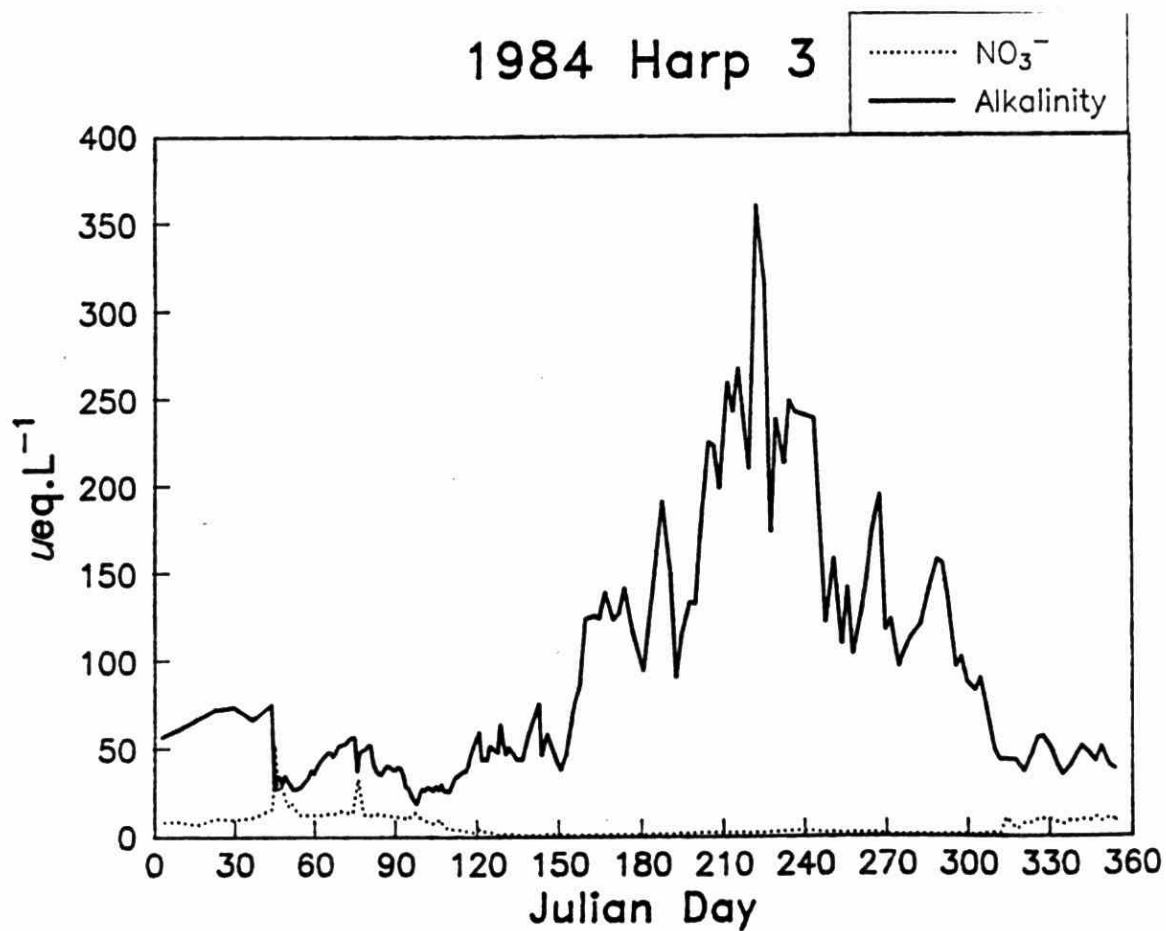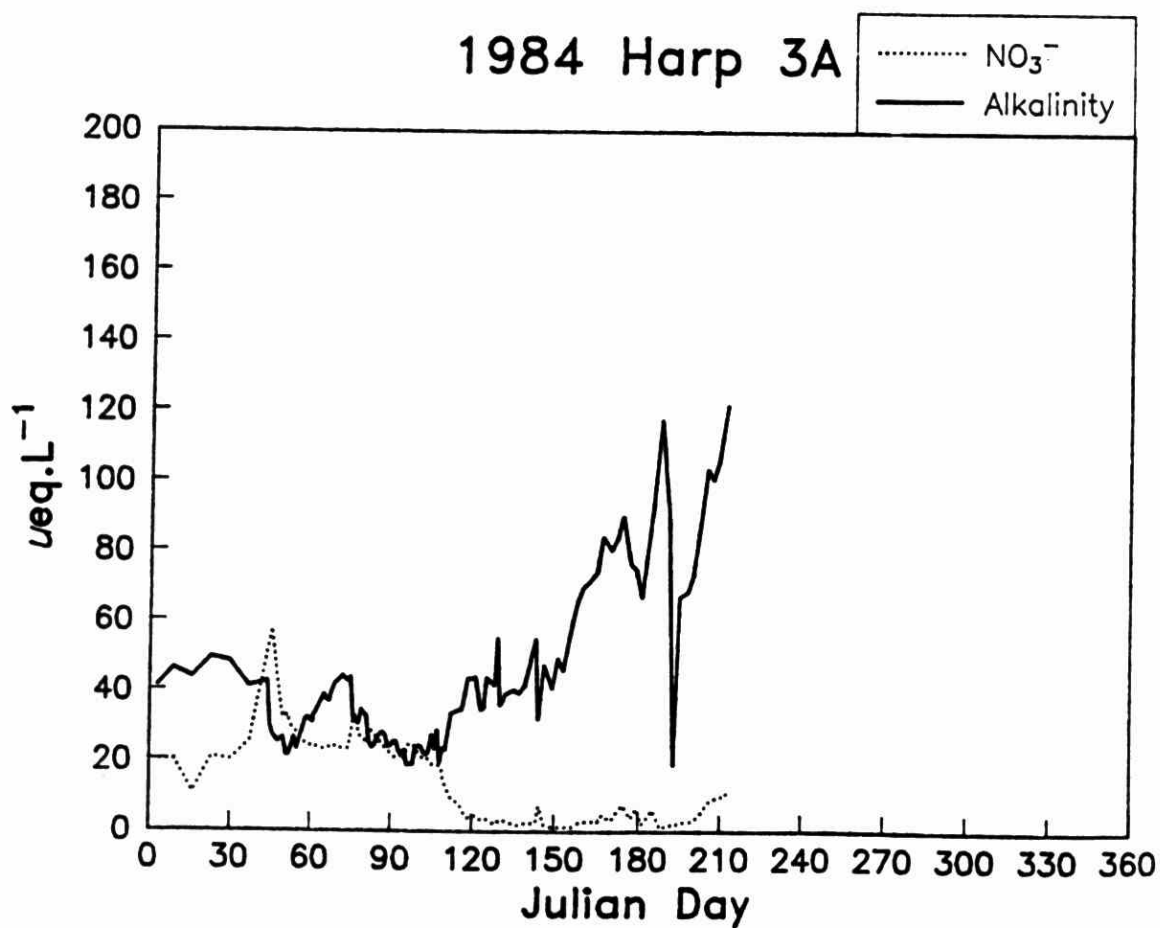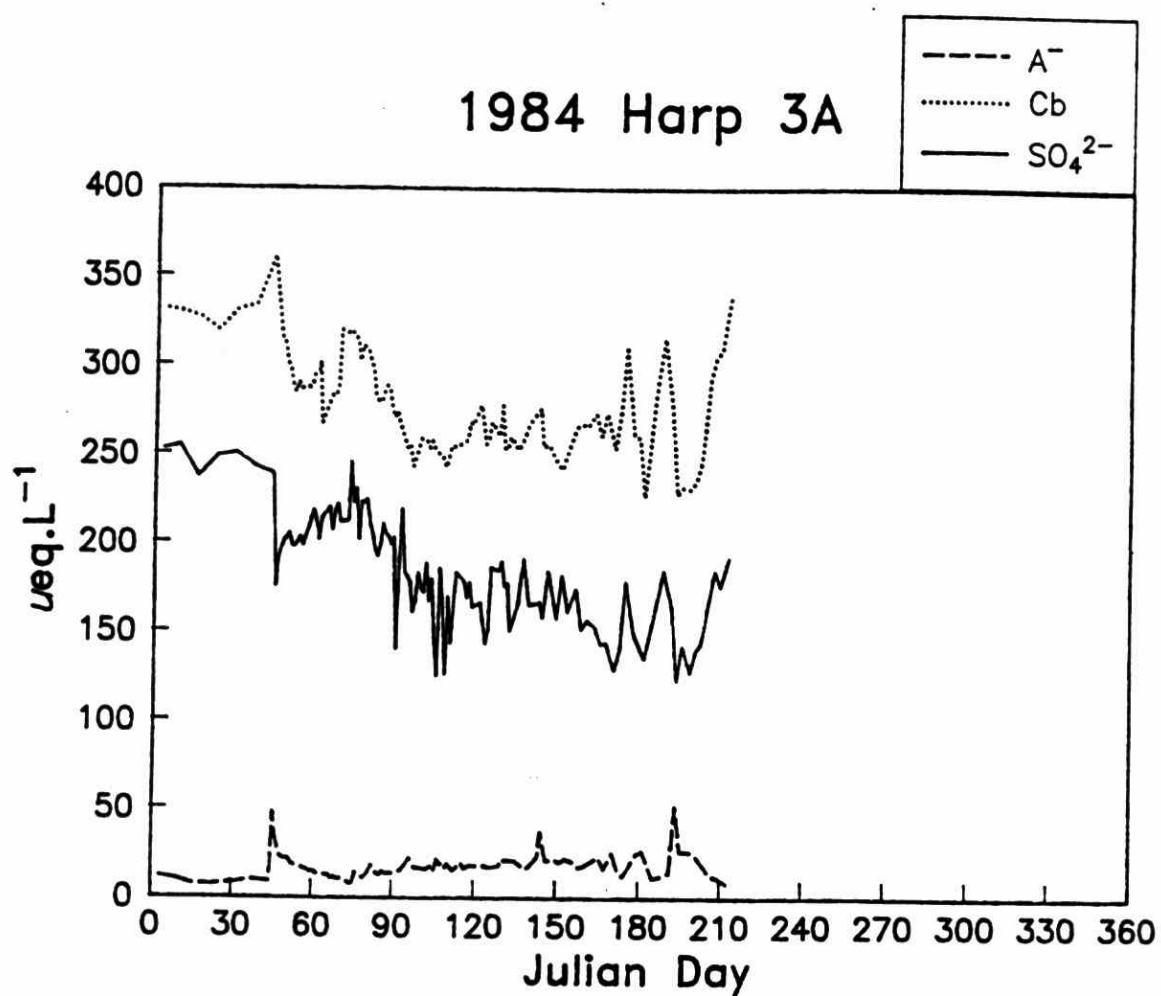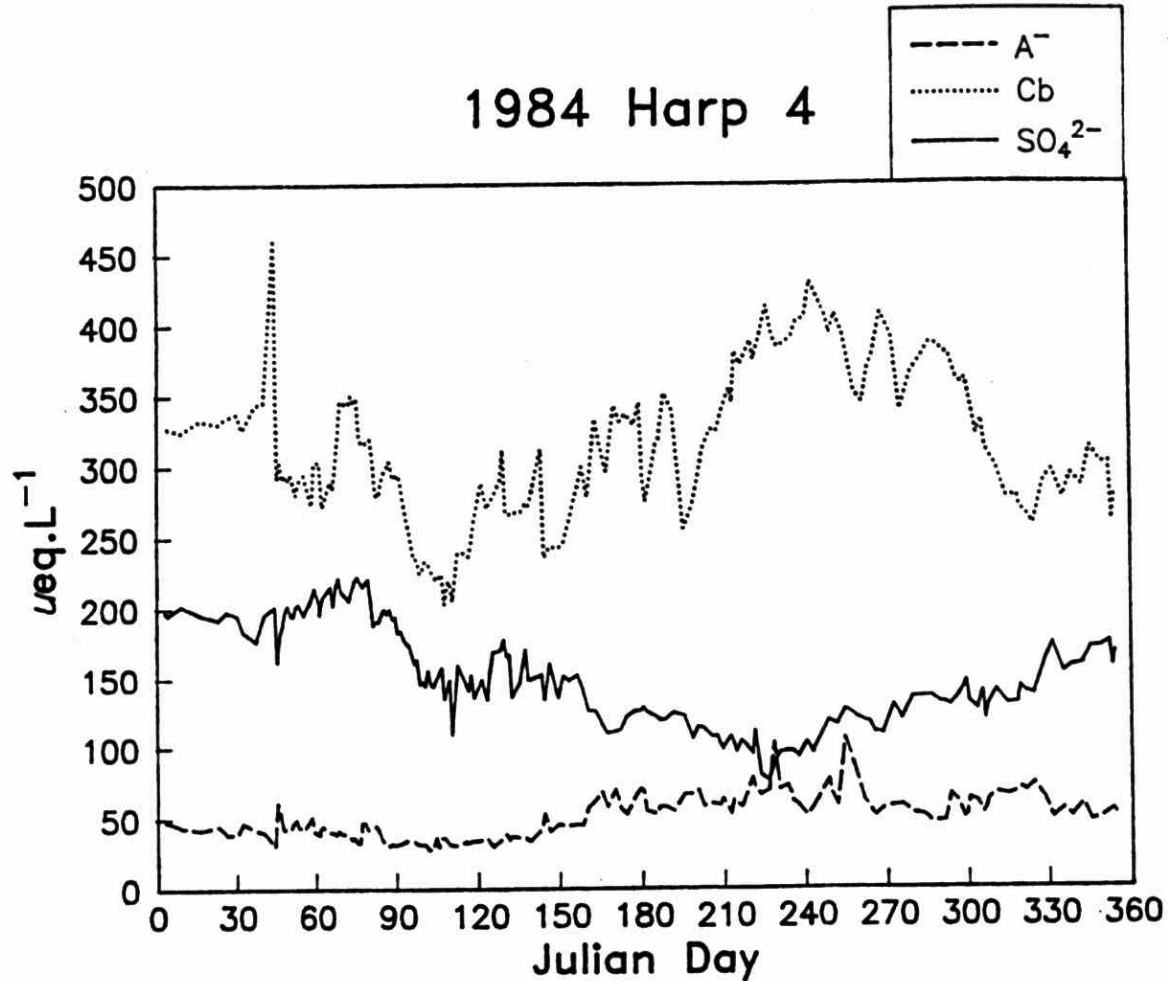
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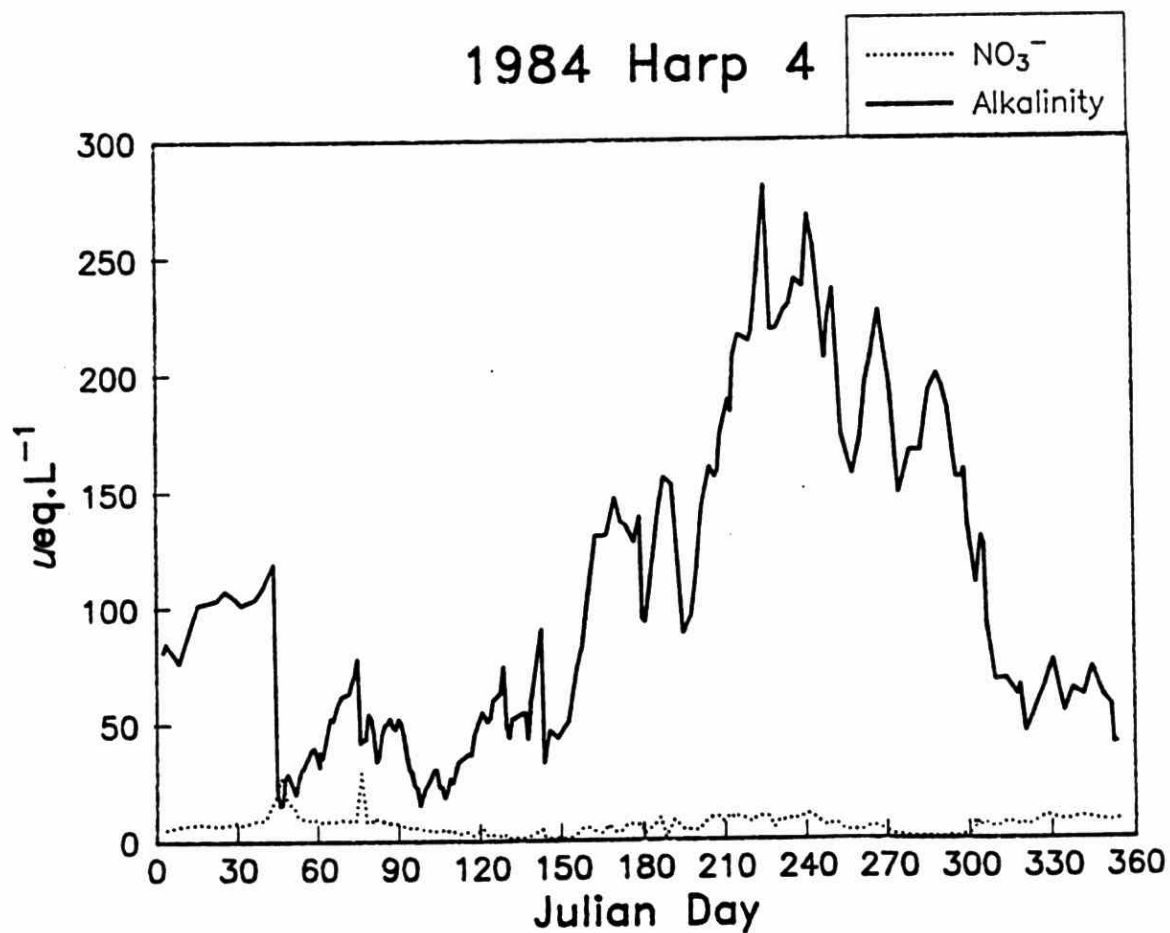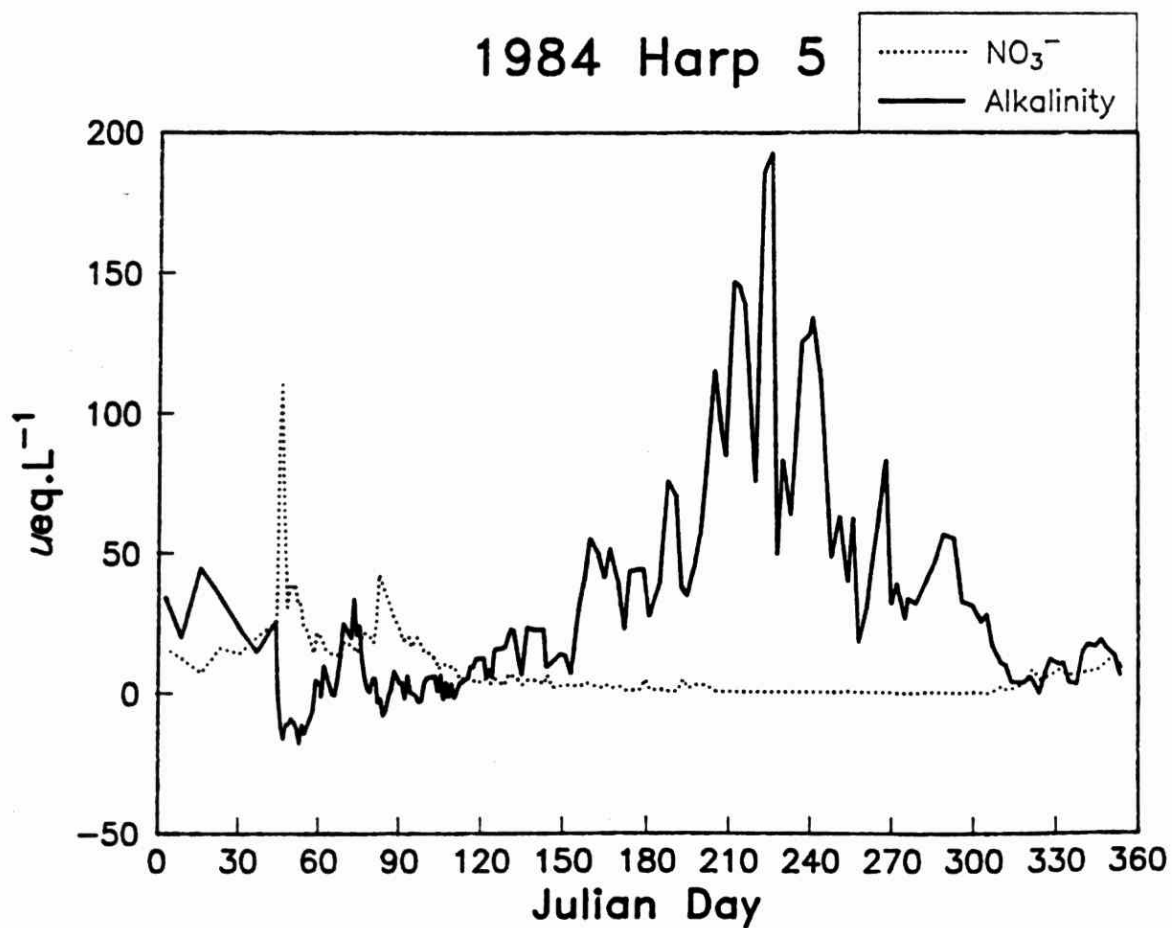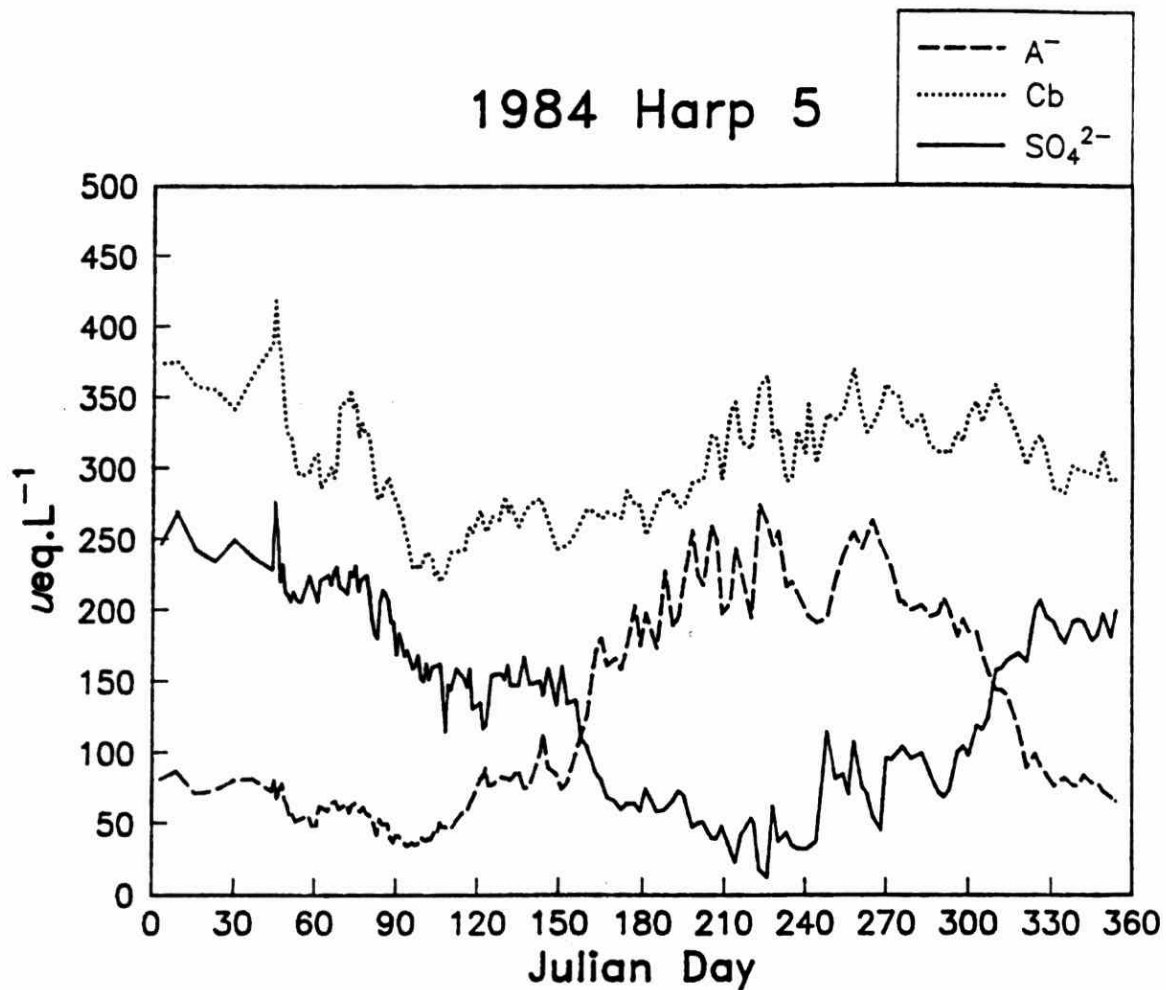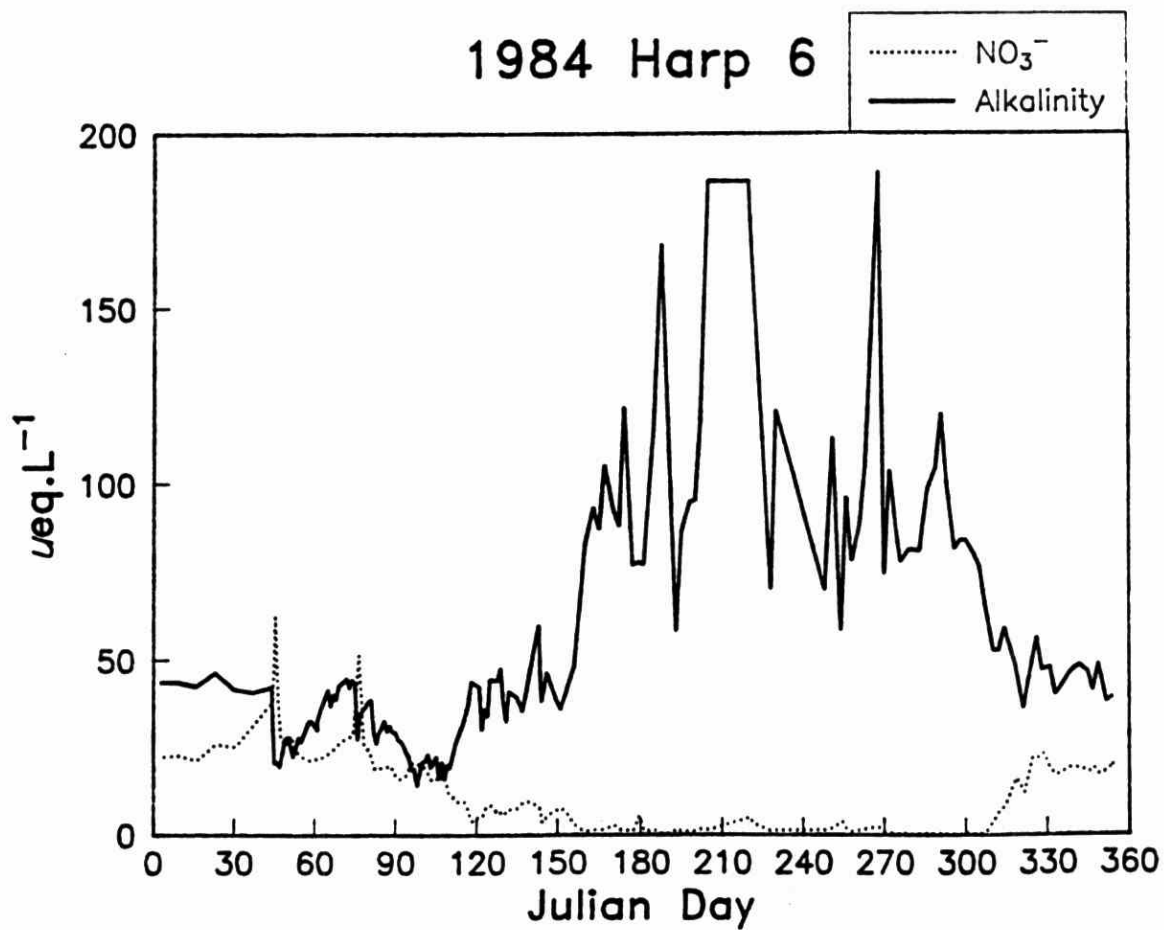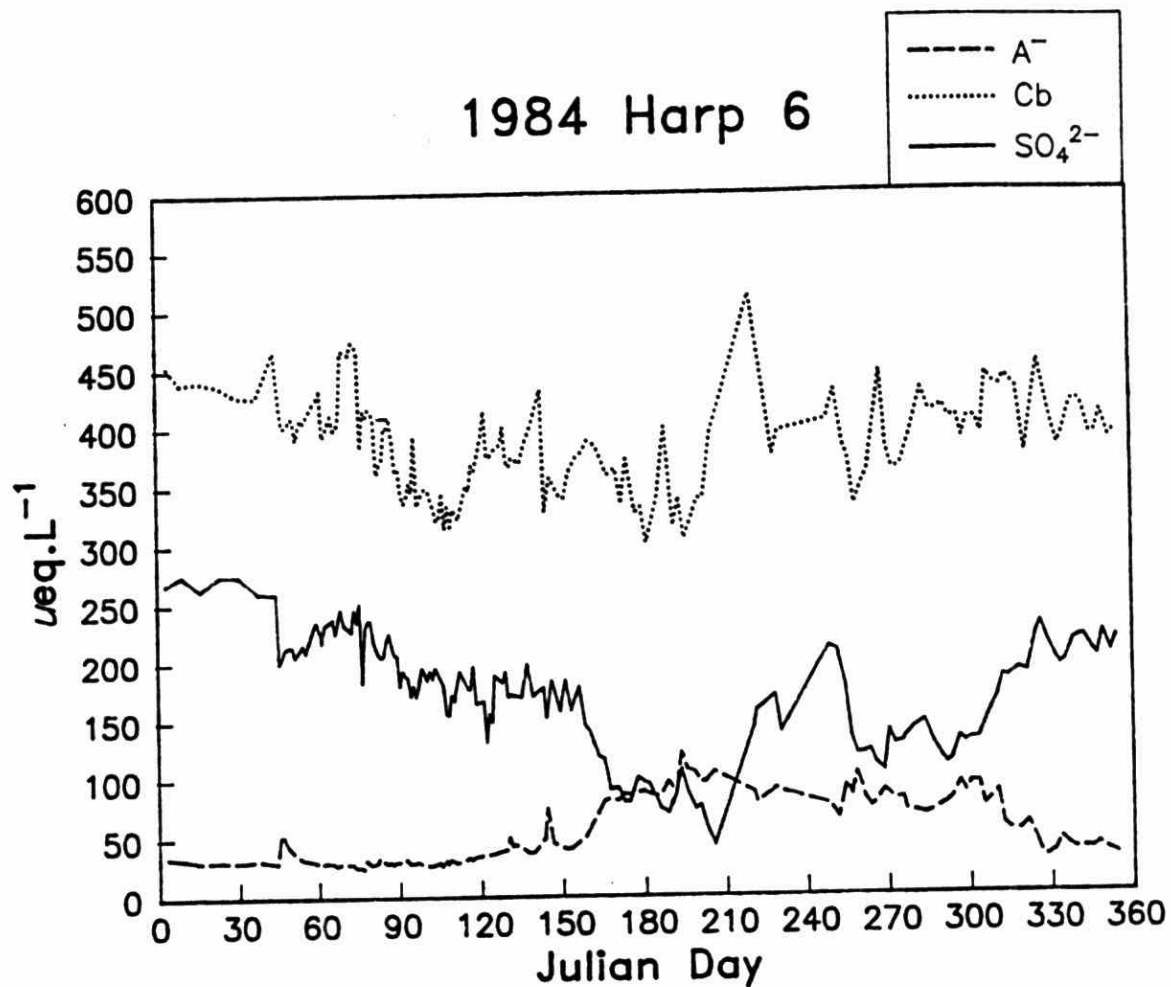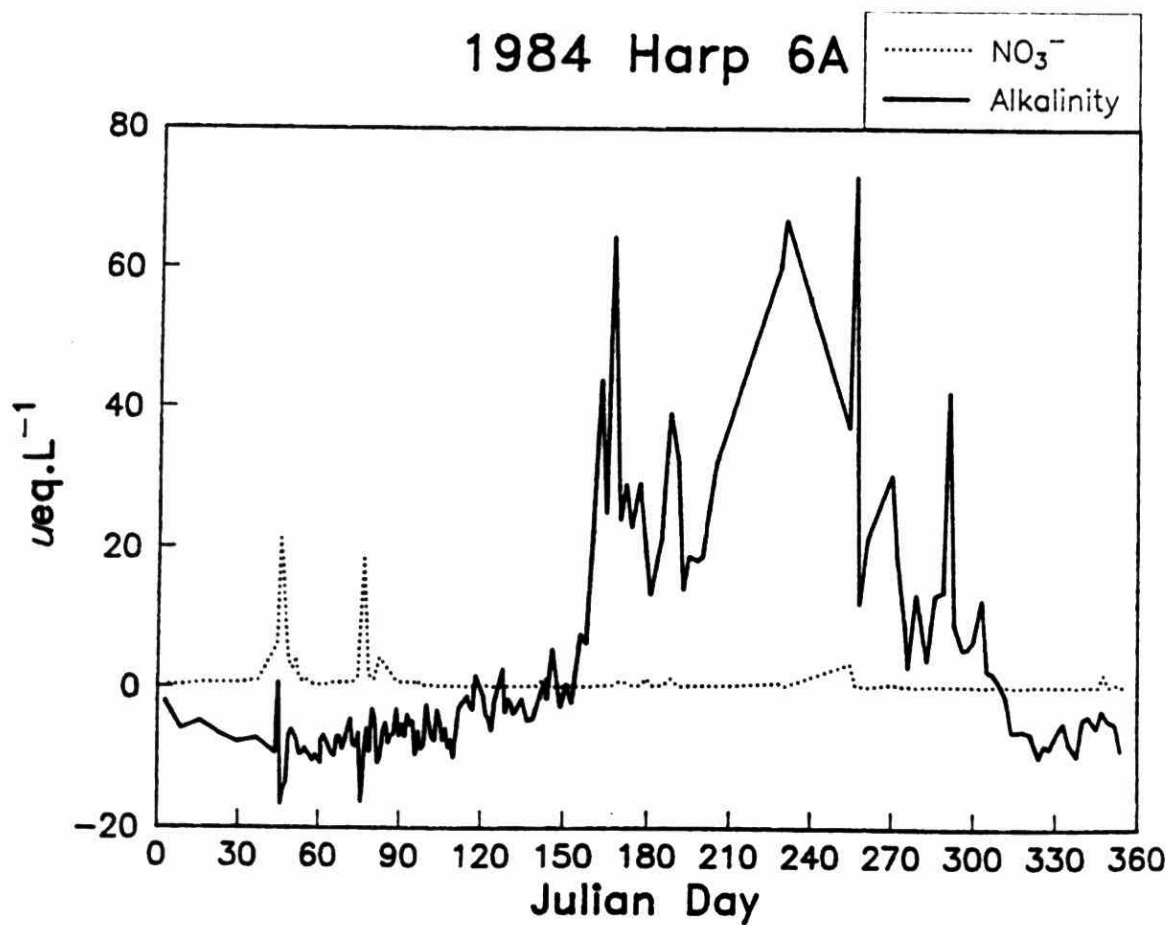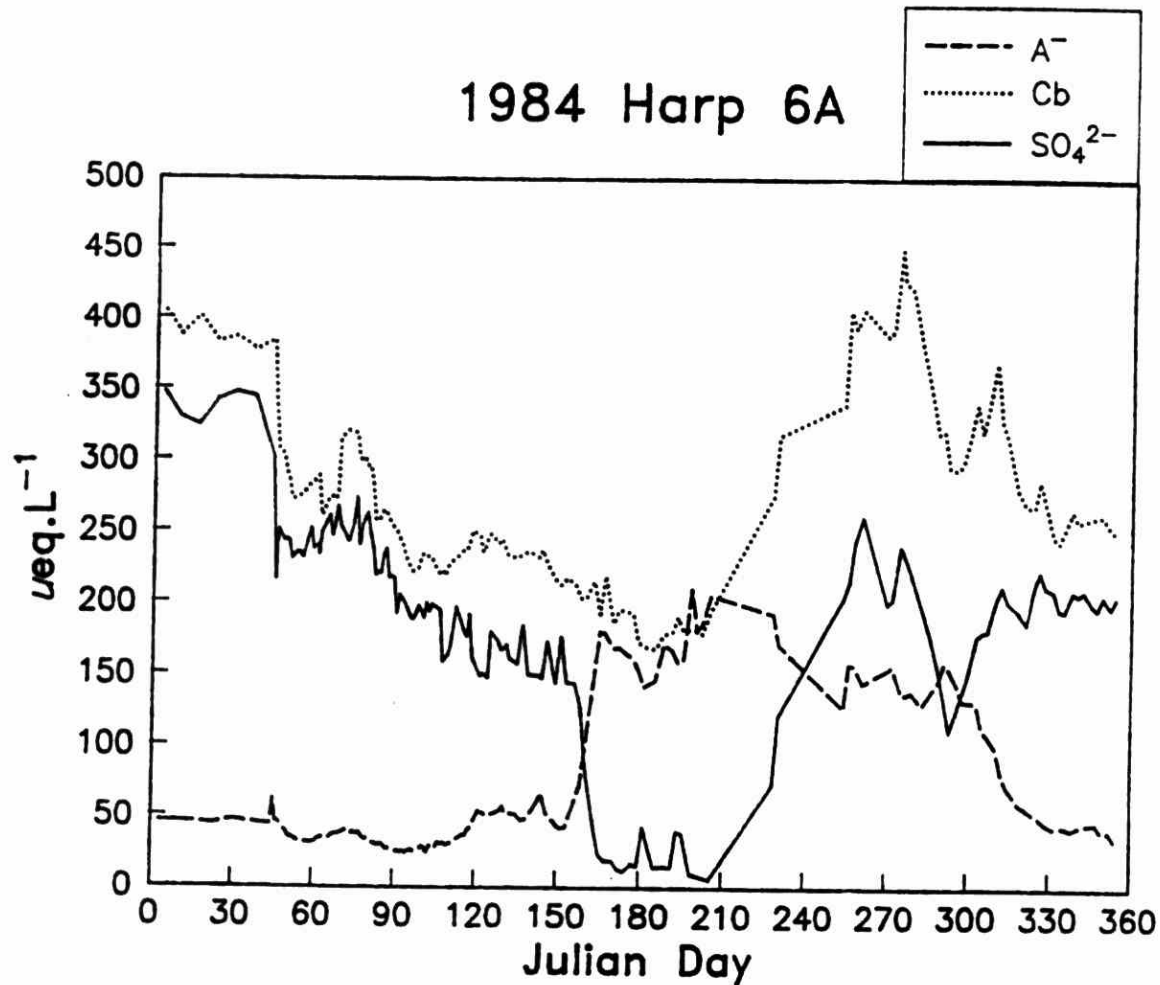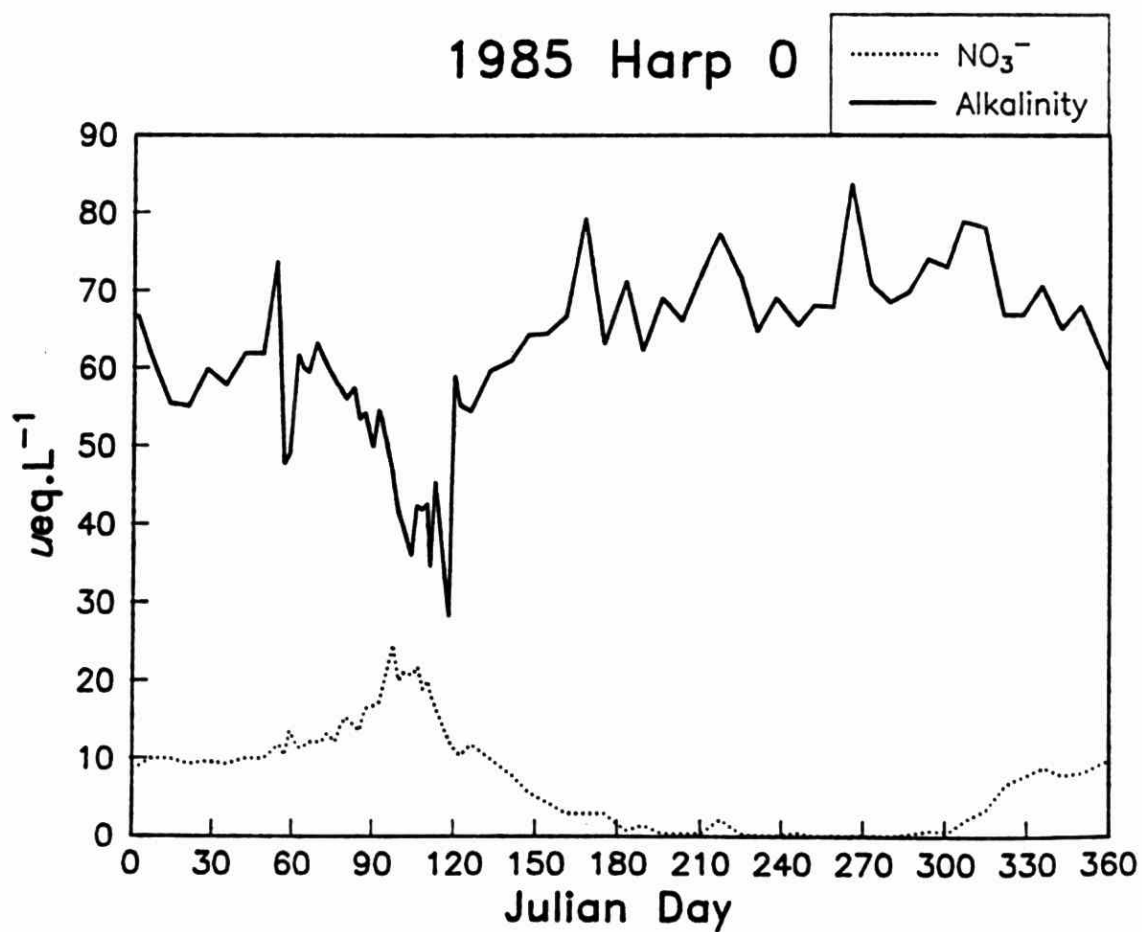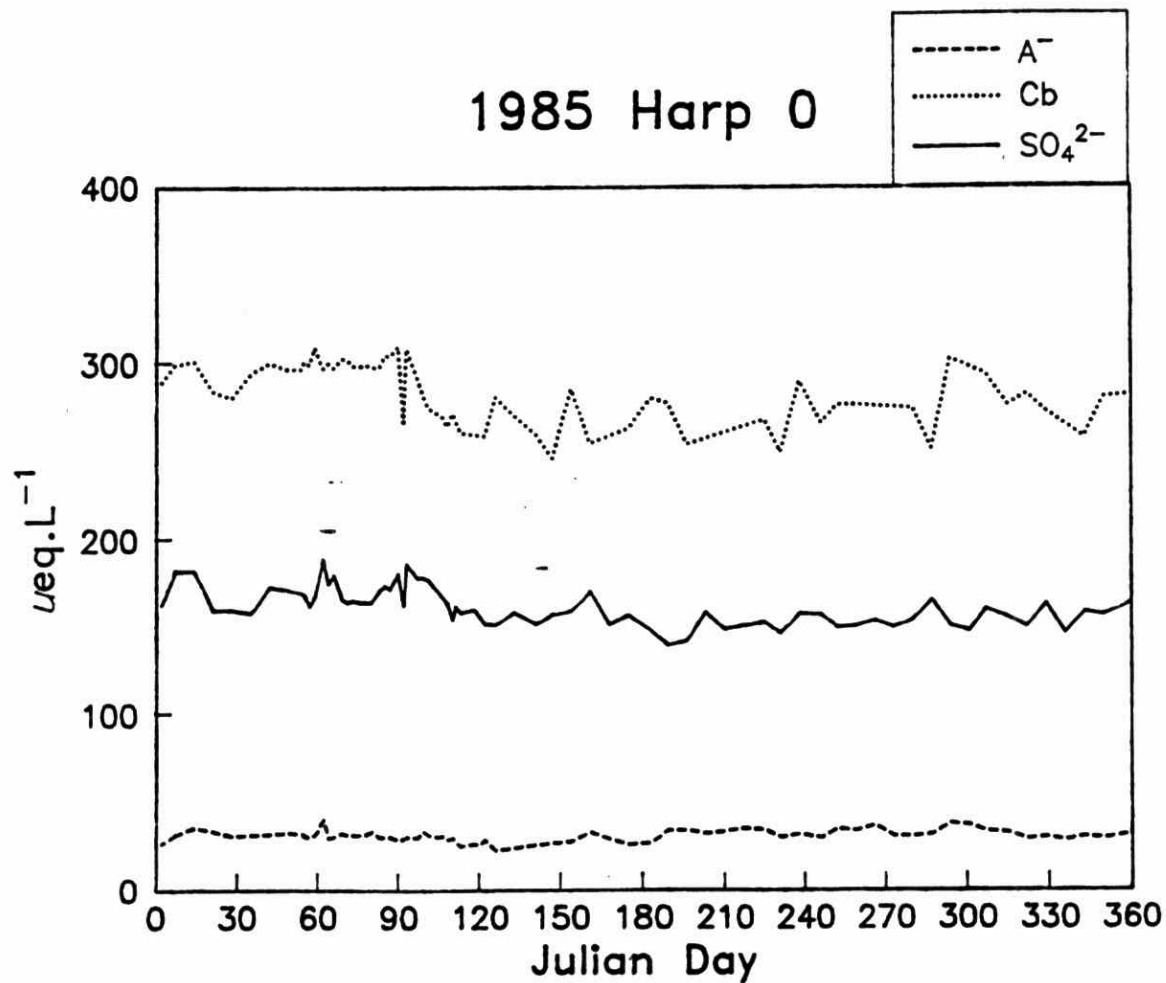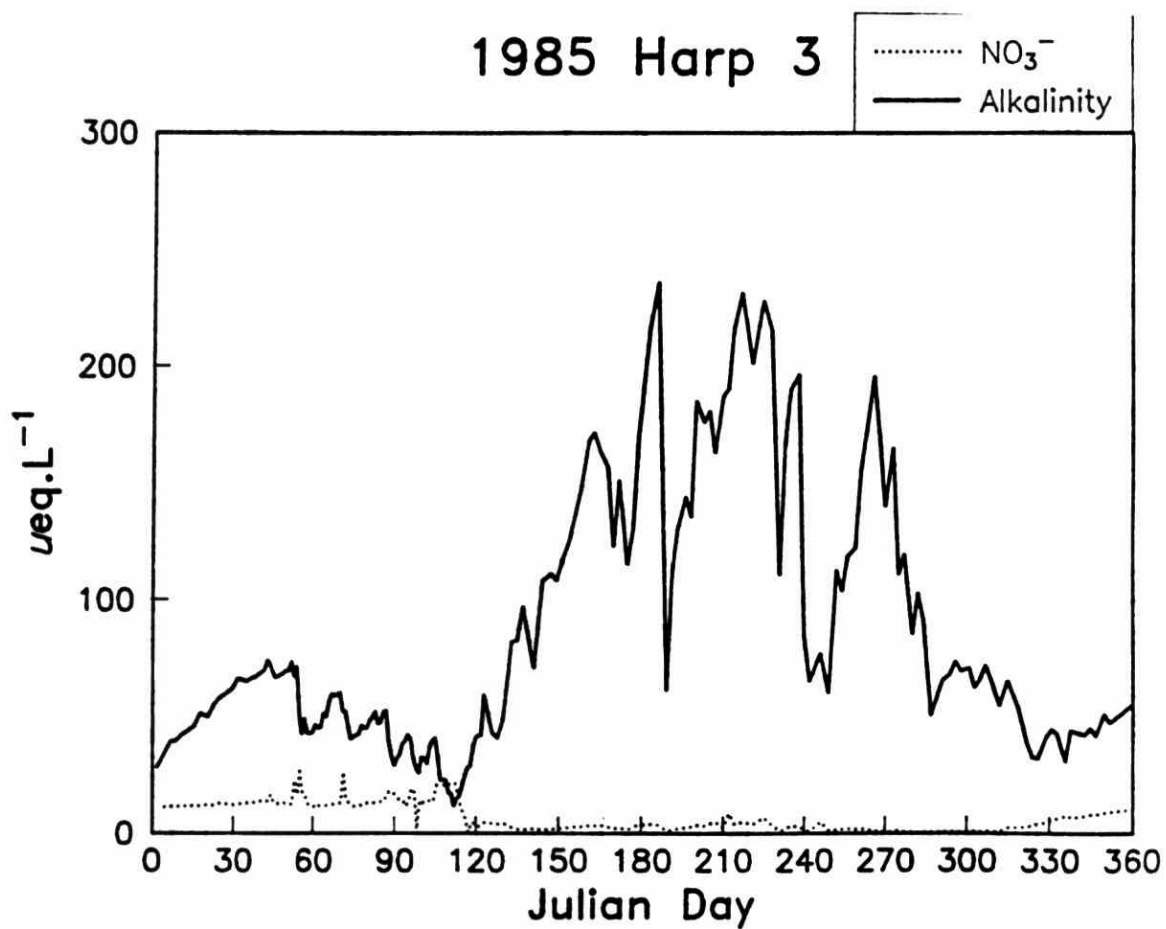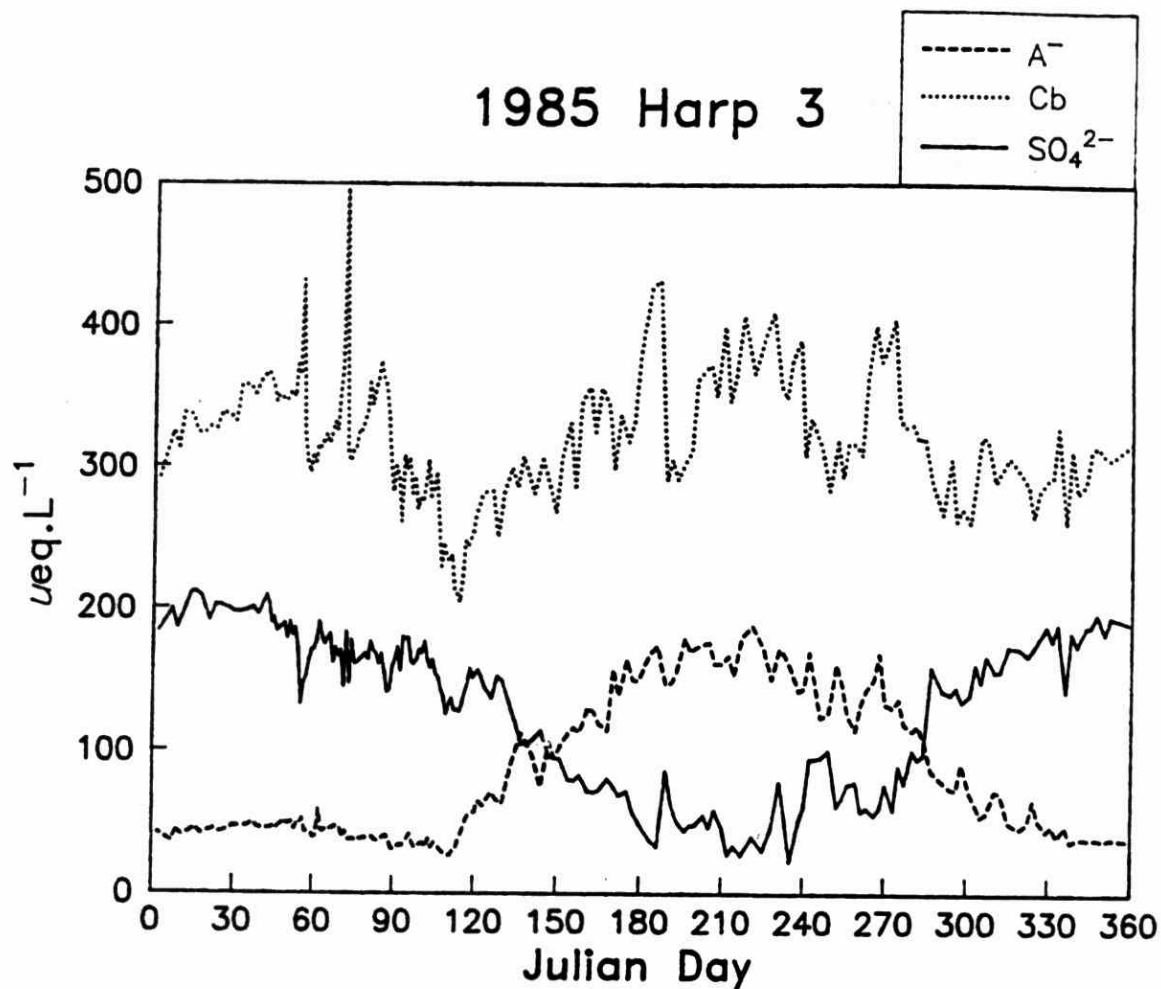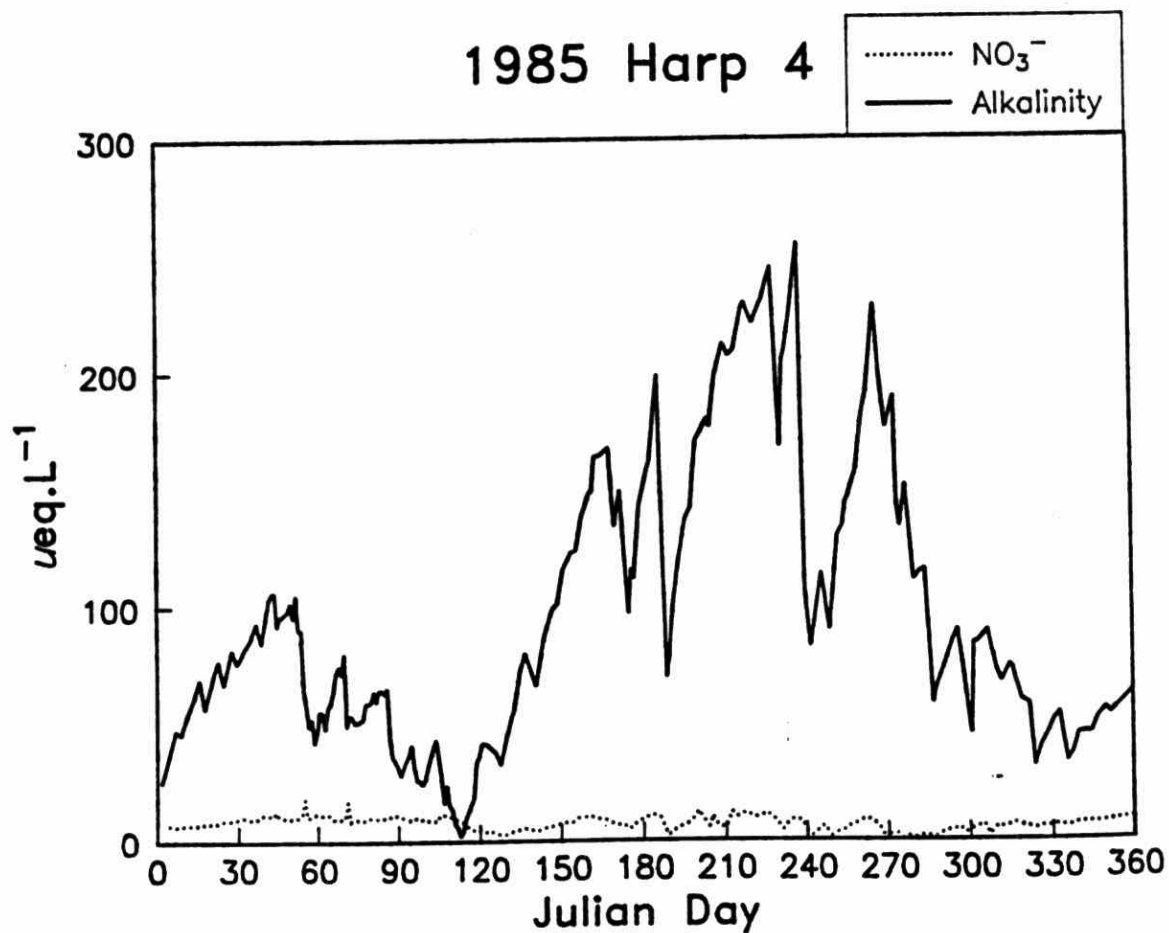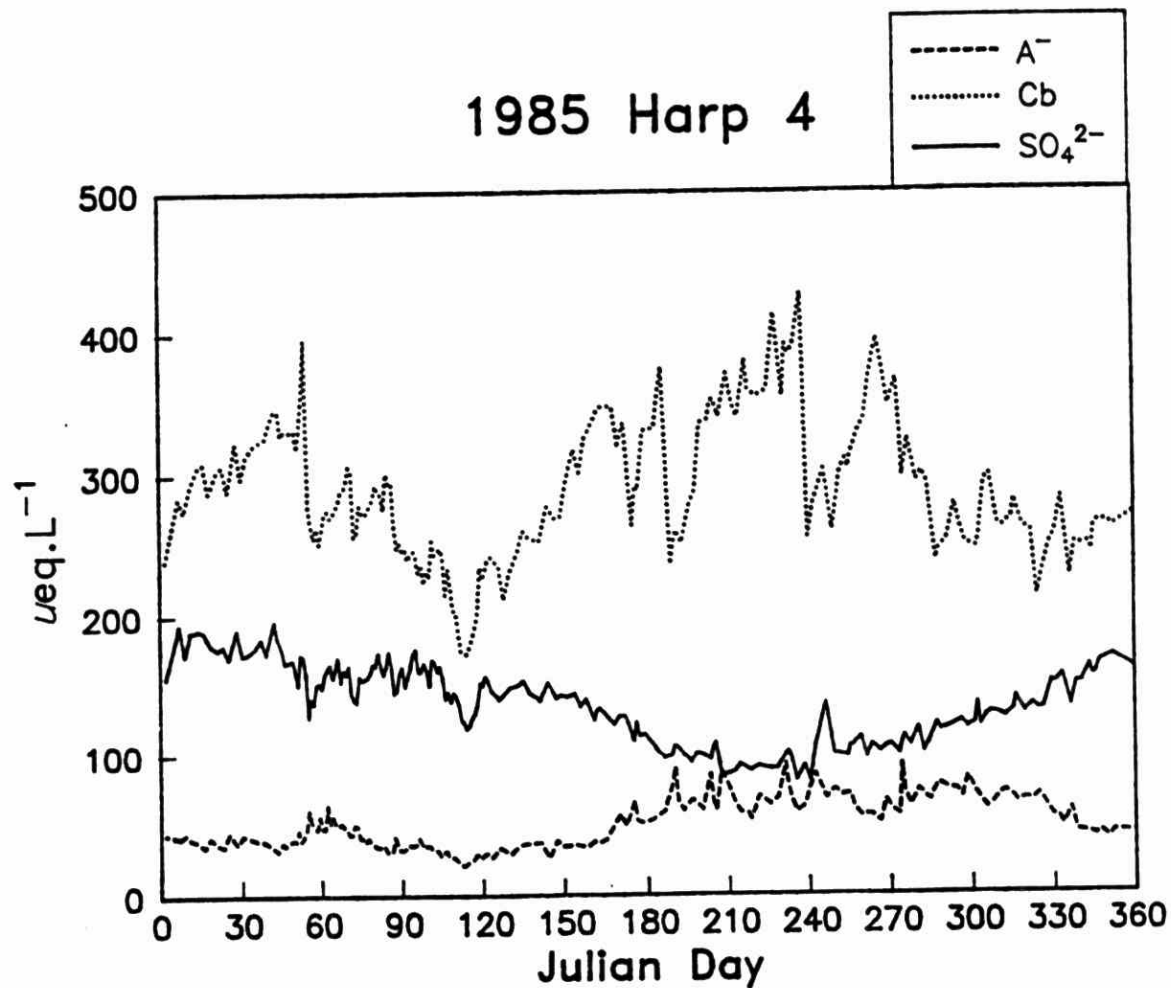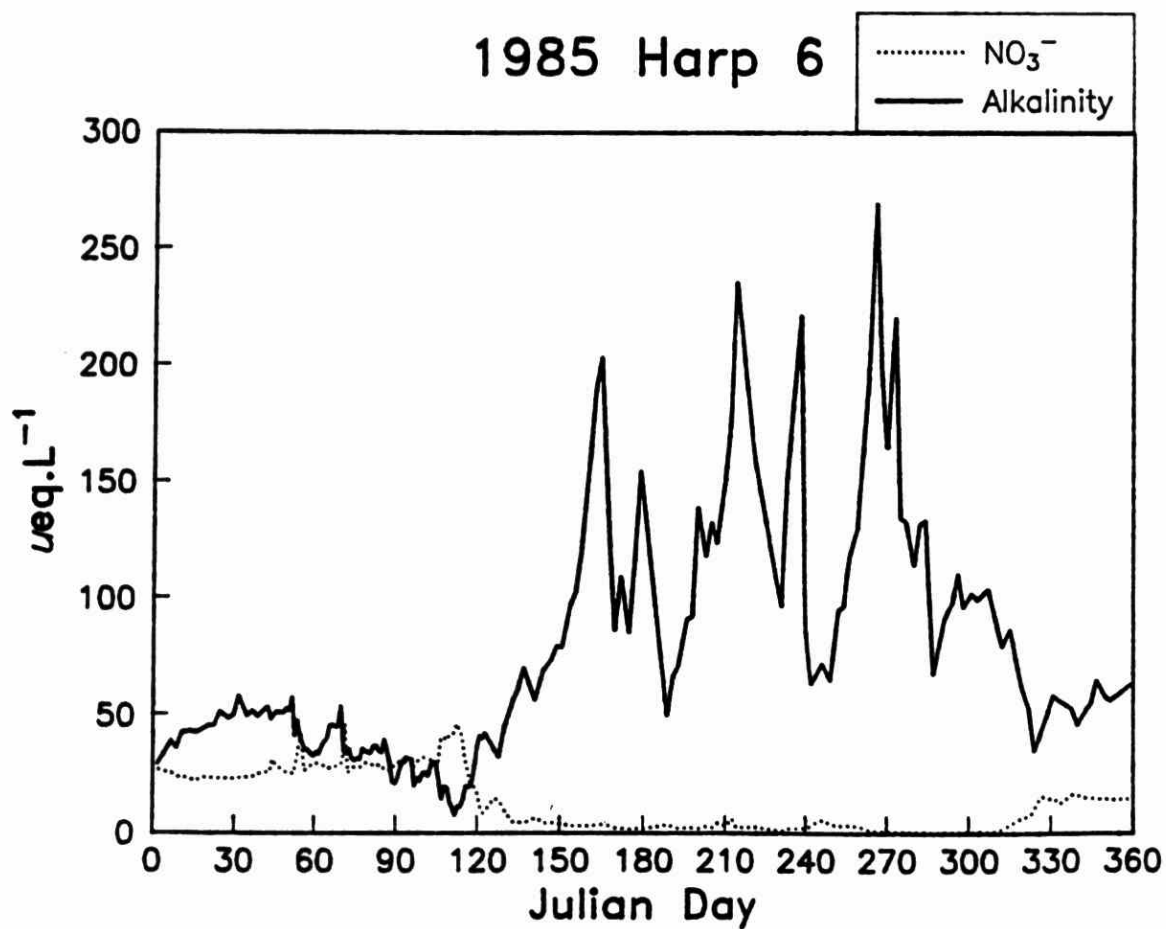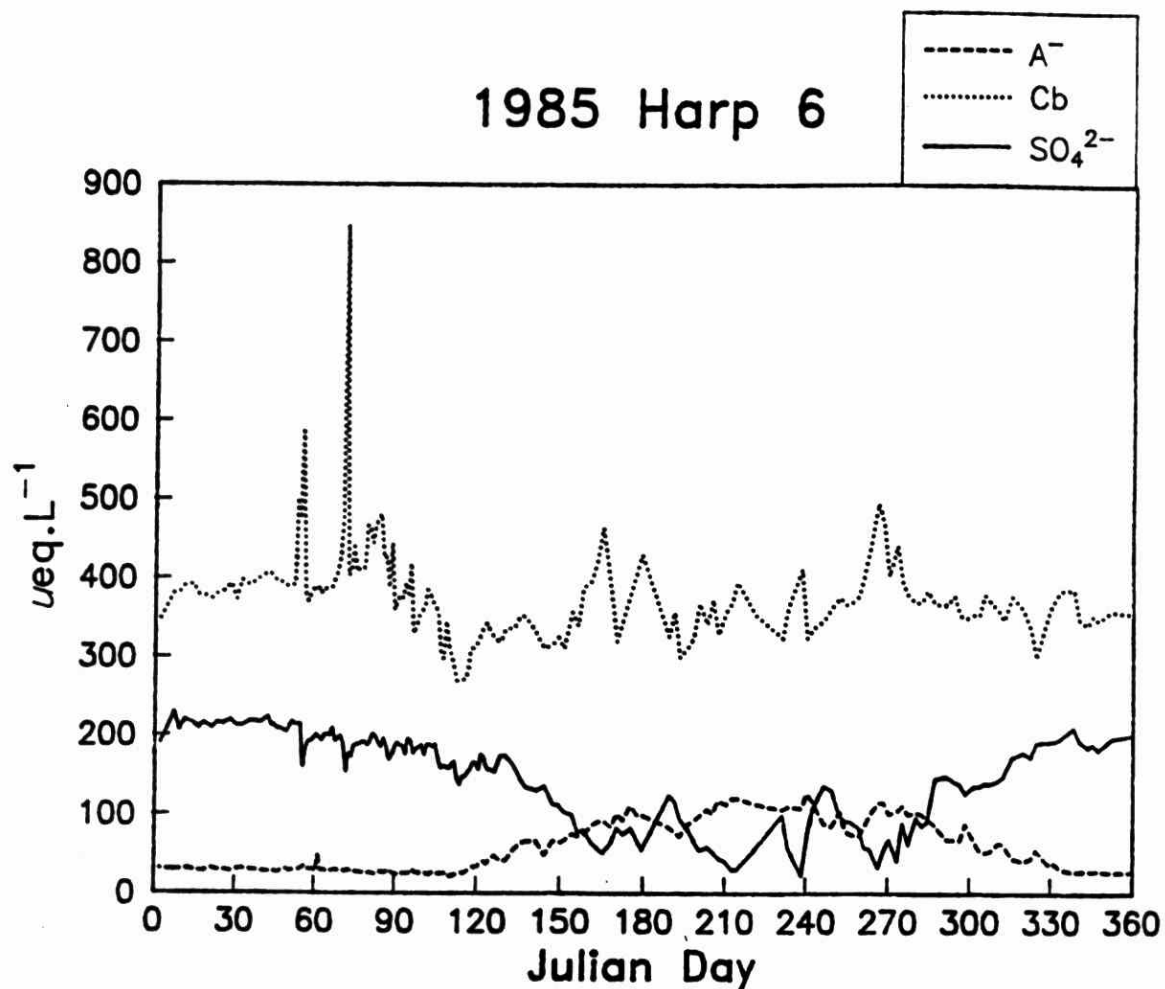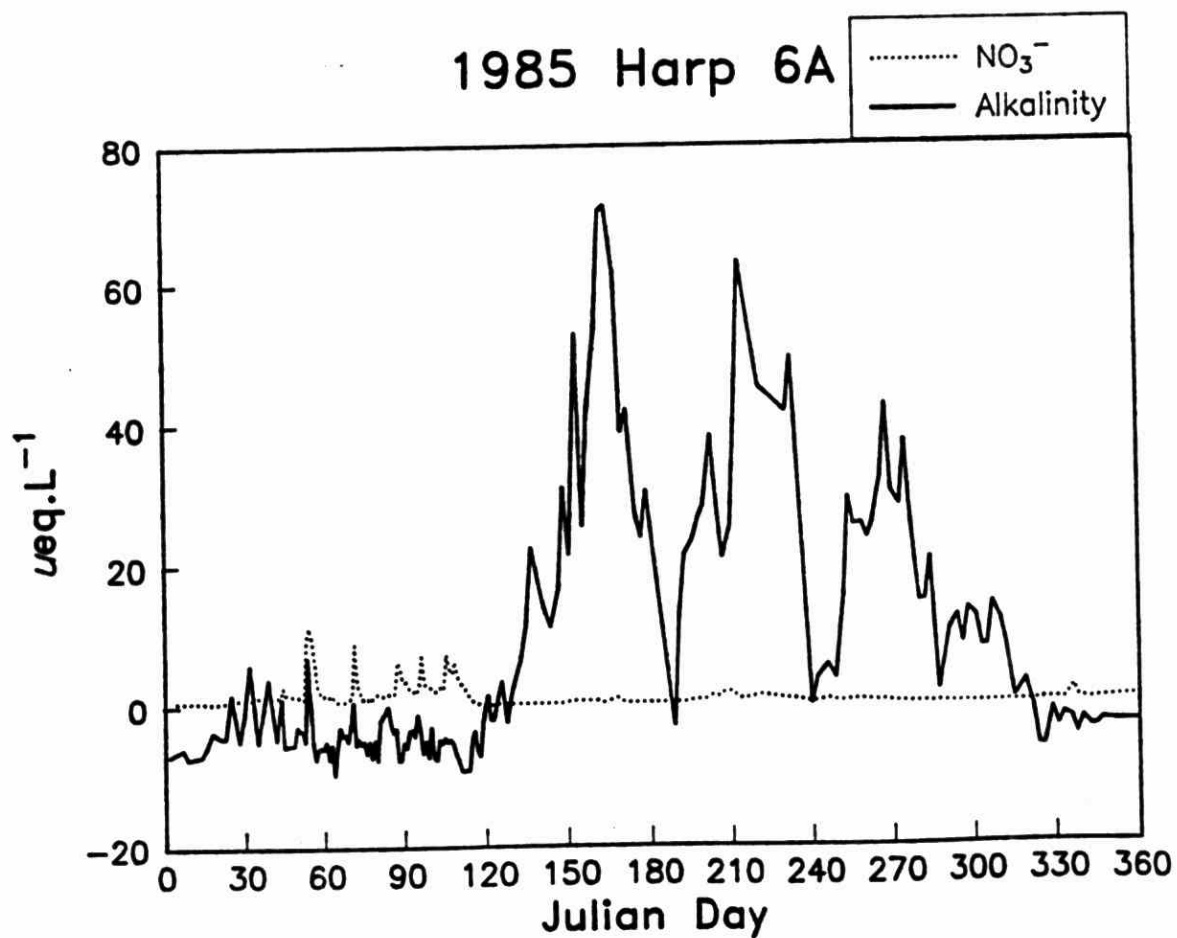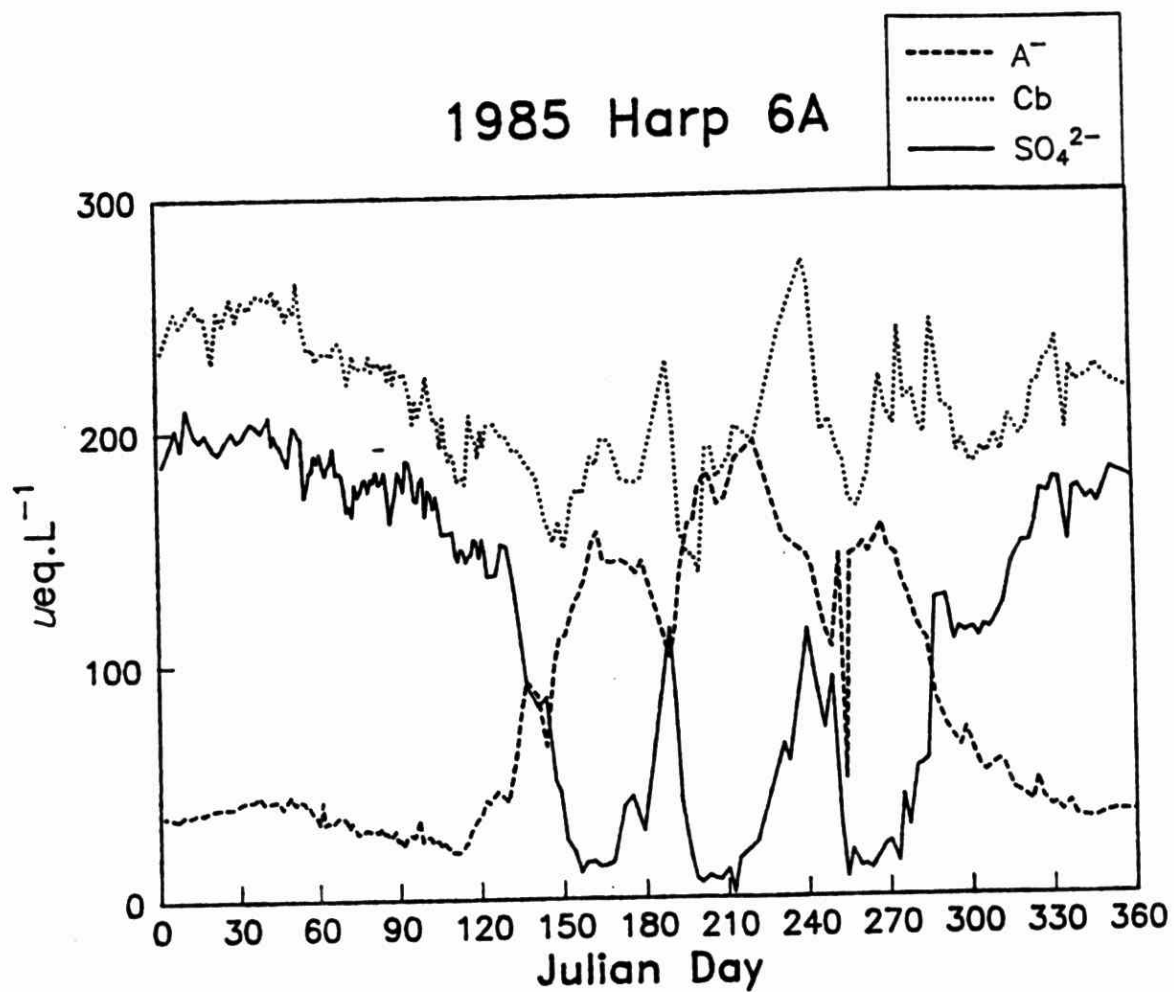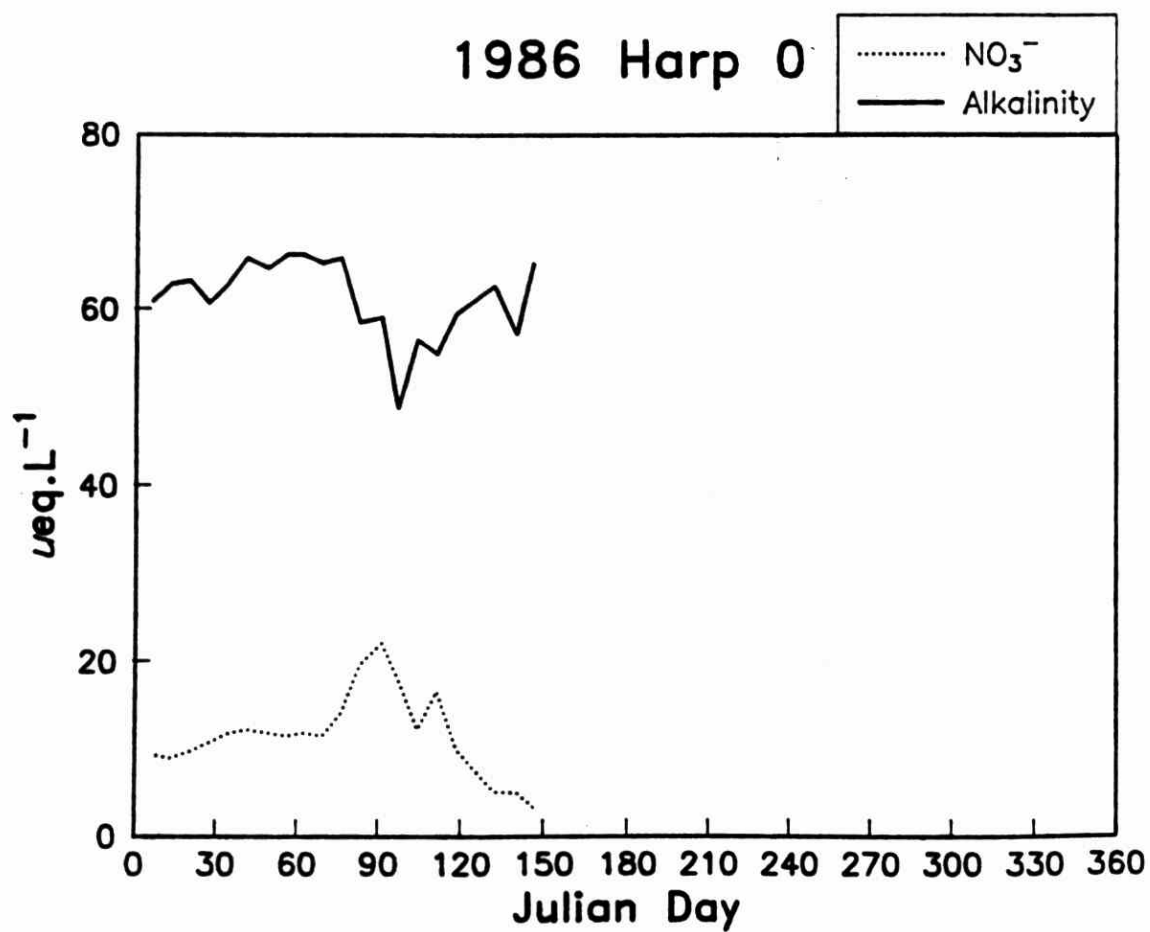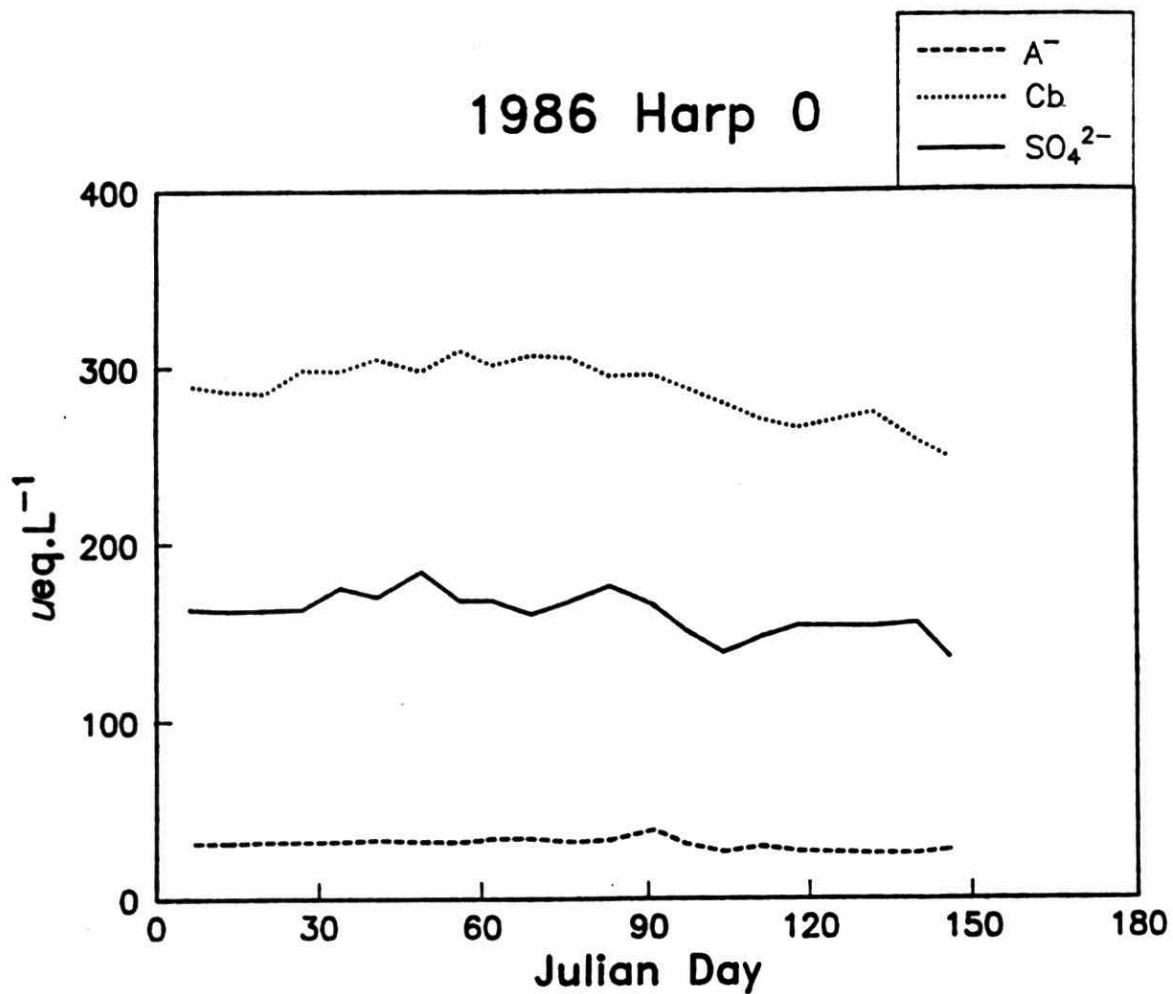
1986 Harp 0

1986 Harp 3

1986 Harp 3

1986 Harp 4

1986 Harp 4

1986 Harp 5

1986 Harp 5

1986 Harp 6

1986 Harp 6

1986 Harp 6A

1986 Harp 6A

1984 Plastic 0

1984 Plastic 0

1985 Plastic 0

1985 Plastic 0

1985 Plastic 1

1985 Plastic 1

1986 Plastic 0

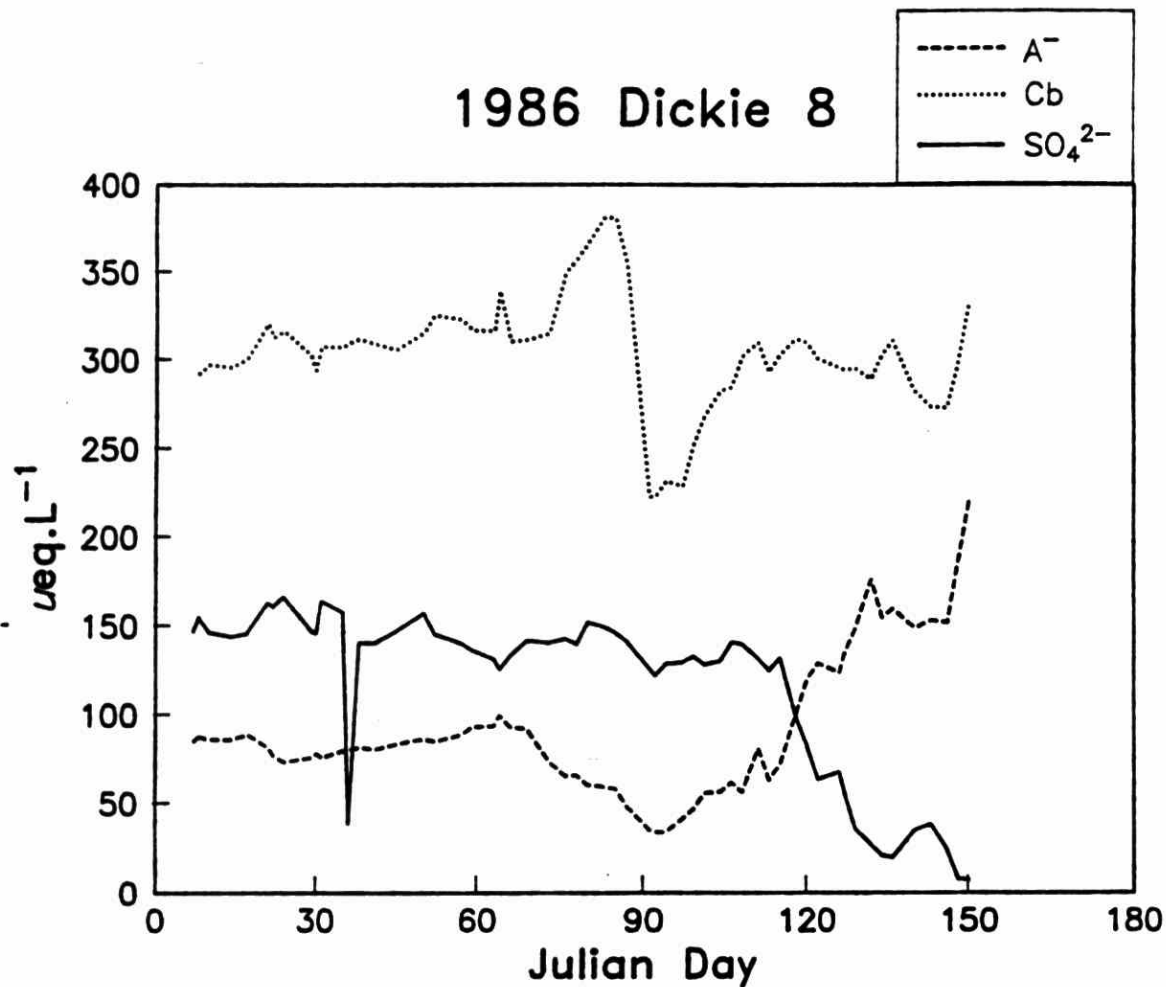1986 Plastic 0

1986 Plastic 1

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1984 Dickie 0

1984 Dickie 0

1984 Dickie 5

1984 Dickie 5

1984 Dickie 6

1984 Dickie 6

1984 Dickie 8

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1984 Dickie 10

1984 Dickie 10

1984 Dickie 11

1984 Dickie 11

1985 Dickie 0

1985 Dickie 0

1985 Dickie 5

1985 Dickie 5

1985 Dickie 6

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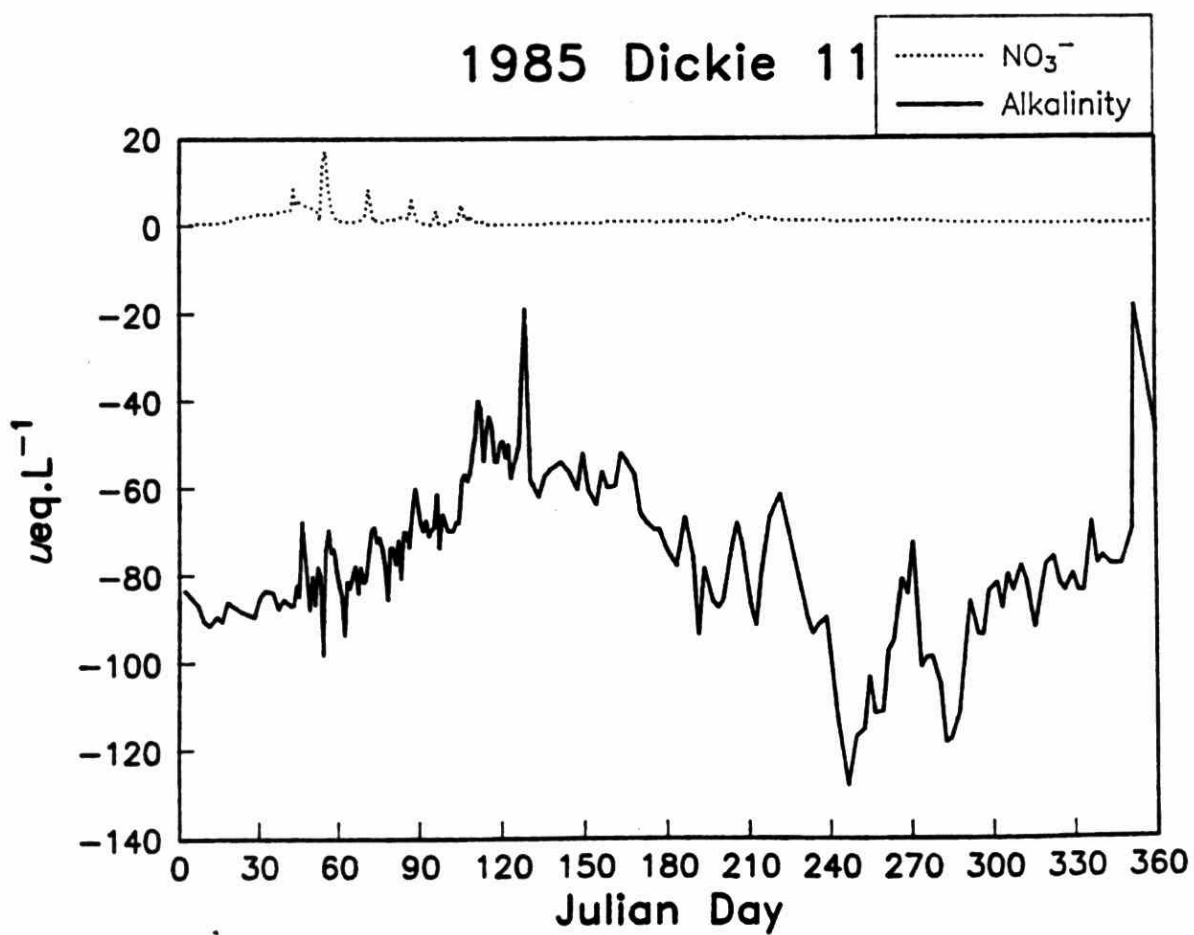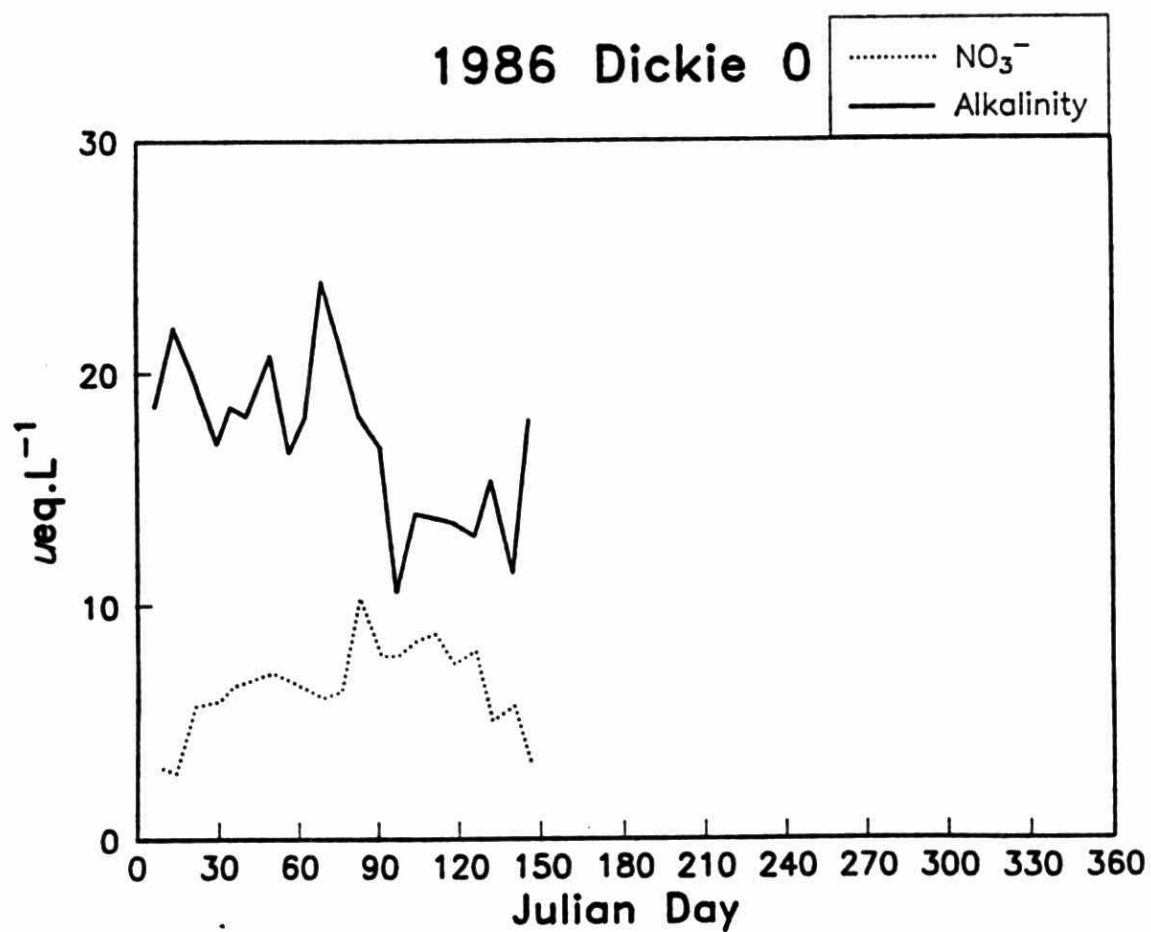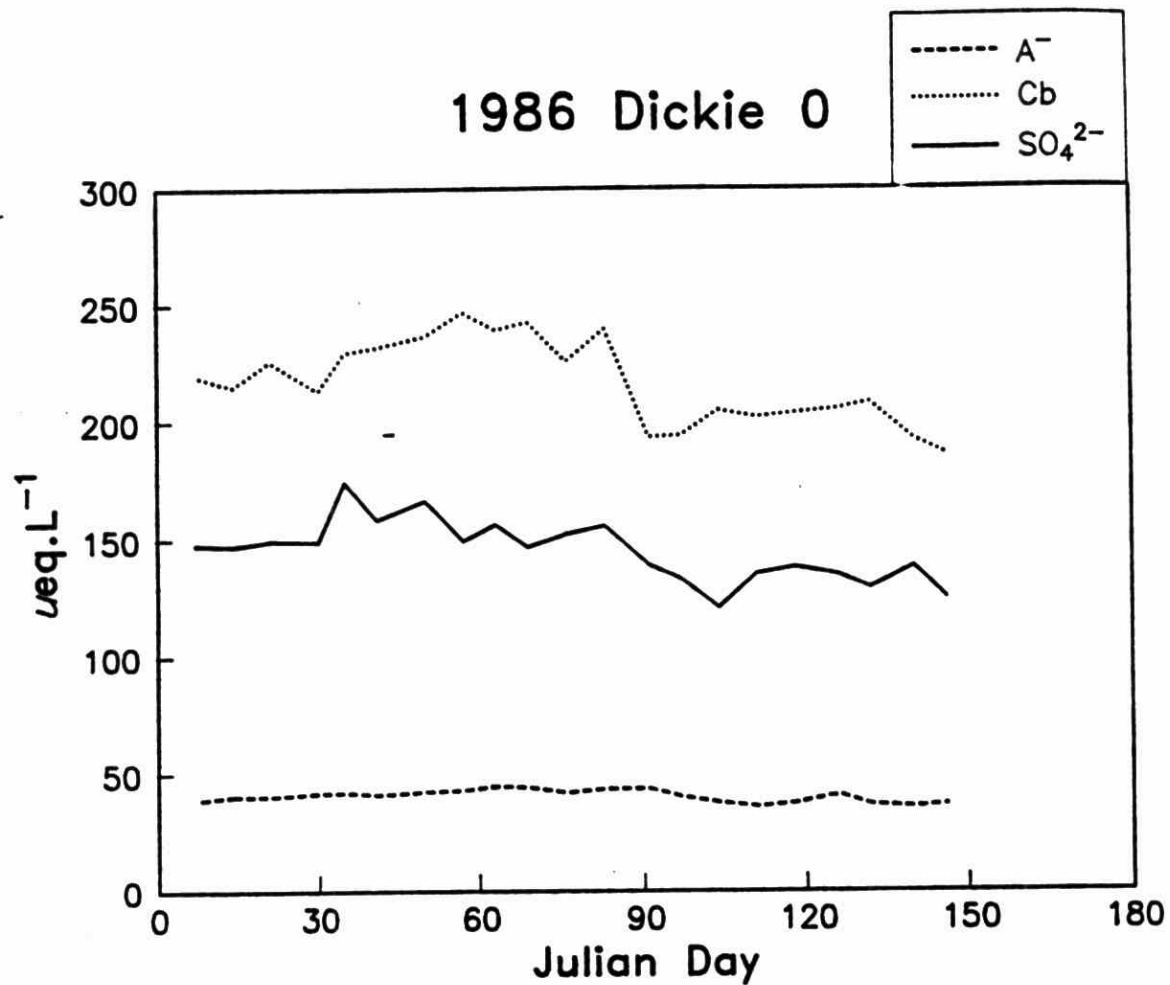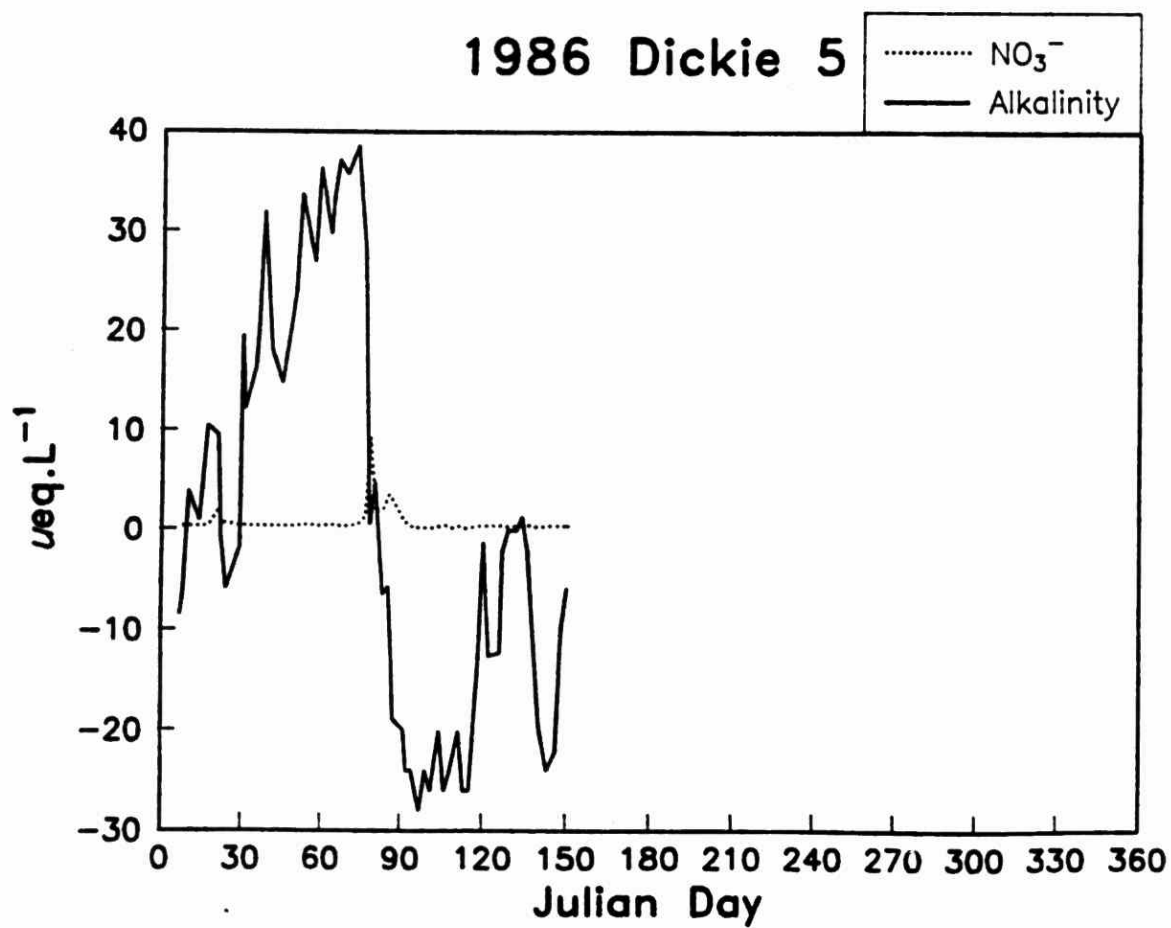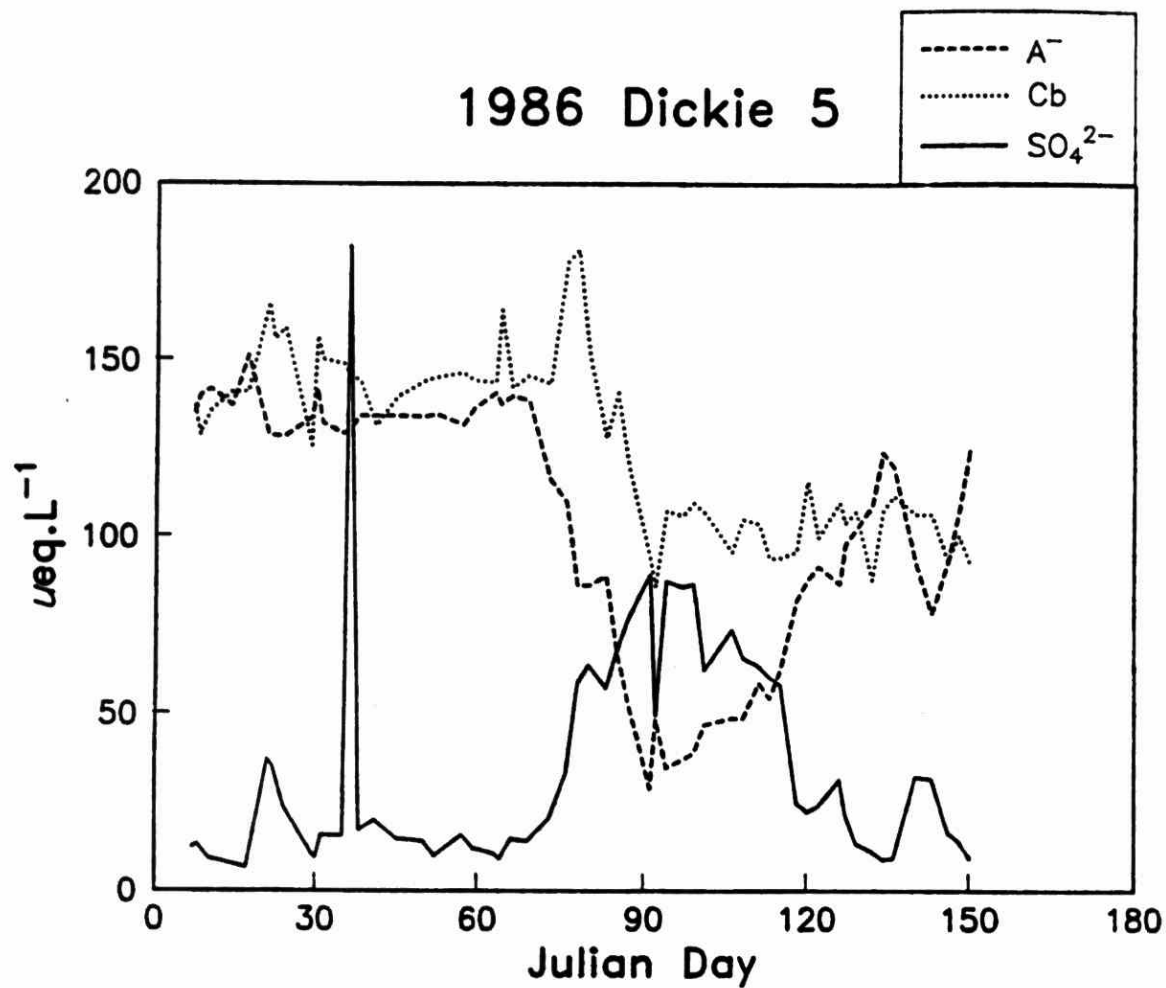
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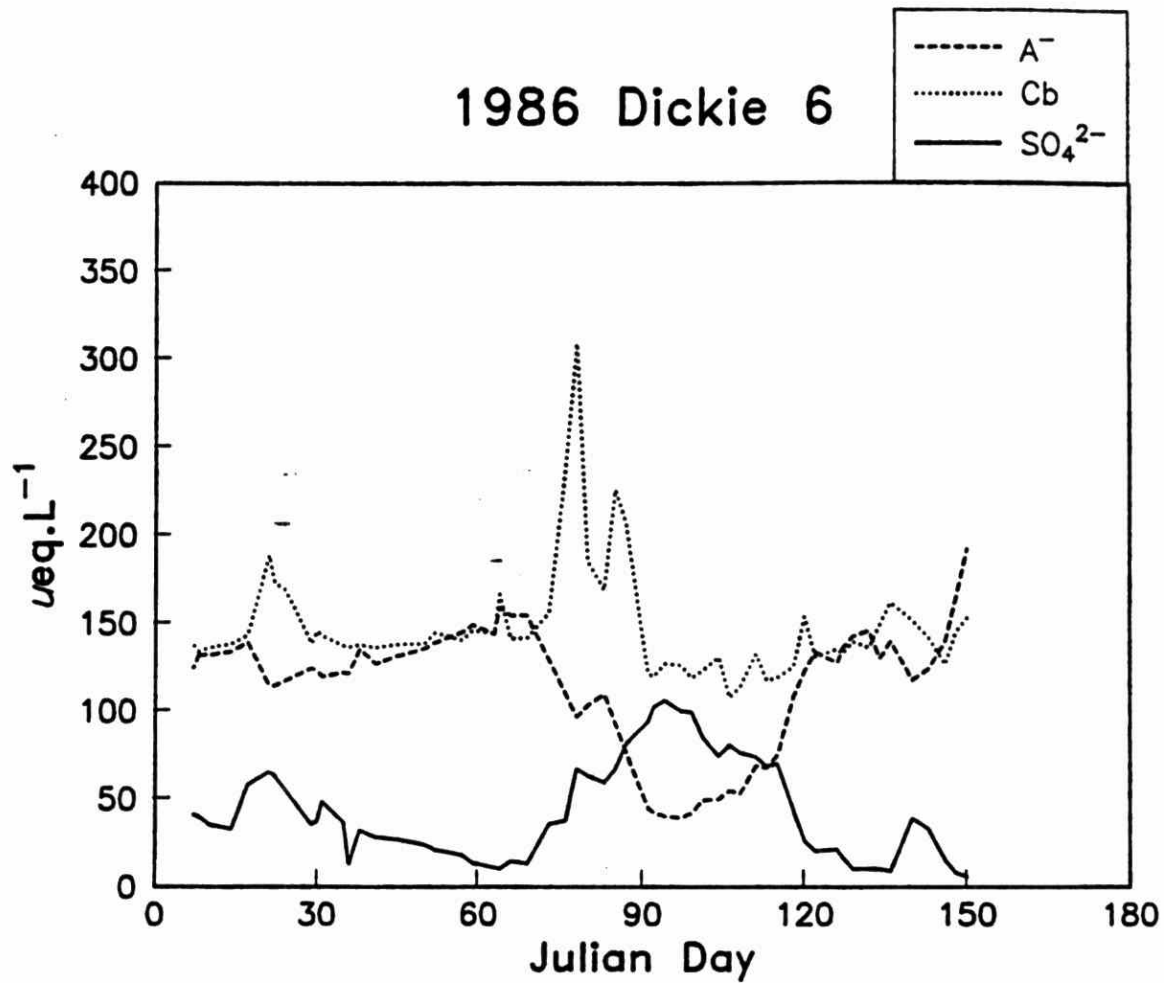
1986 Dickie 6

1986 Dickie 6

1986 Dickie 8

1986 Dickie 8

1986 Dickie 10

1986 Dickie 10

1986 Dickie 11

1986 Dickie 11